FRUSTRATED LEWIS PAIRS: A CONCEPT FOR SMALL MOLECULE ACTIVATION AND HYDROGENATION CATALYSIS

DISSERTATION

zur

Erlangung der naturwissenschaftlichen Doktorwürde

(Dr. sc. nat.)

vorgelegt der

Mathematisch-naturwissenschaftlichen Fakultät

der

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Zürich 2010

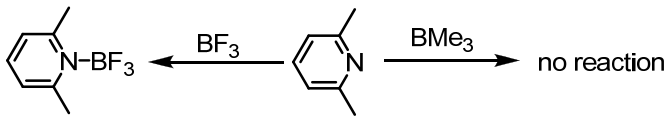
To my family

Contents

Introduction

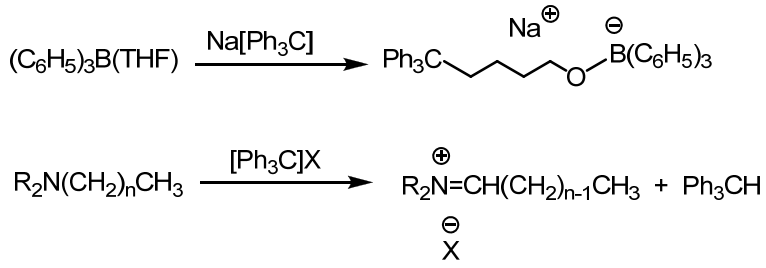
The description of "electronic" acids and bases put forth by Gilbert N. Lewis in 1923 categorizing molecules as electron-pair acceptors (Lewis acids) and electron-pair donors (Lewis bases) is one of the fundamental concepts in Inorganic Chemistry.[1] A Lewis acid is characterized by a low-lying "lowest unoccupied molecular orbital" (LUMO), which can interact with the lone electron-pair in the high-lying "highest occupied molecular orbital" (HOMO) of a Lewis base. Therefore, a primary consequence of this concept of chemical reactivity is the notion that combination of Lewis acids and bases result in the formation of Lewis acid-base adducts. For example, the Lewis acid borane (BH_3) combines with the Lewis base ammonia (NH_3) to generate the adduct ammonia-borane, NH_3-BH_3. Actually, the concept of donor - acceptor adduct formation contritubes the basis of transition metal coordination chemistry. The principles of Lewis acidity and basicity also extend to help our understanding of organic, organometallic, solid state chemistry, as well as surface science. It is clear that this concept is indeed a powerful tool for explaining and understanding much of modern chemistry.

Though most of the reactions follow the Lewis principle that Lewis acids combine with Lewis bases resulting in adducts, recent chemical explorations have encountered some systems that apparently deviate from this principle, because of the steric congestions. Steric hindrance precludes the formation of simple Lewis acid-base adducts, rather enable unusual reactions. In 1942, H. C. Brown and co-workers examined the interaction of pyridines with simple boranes found that lutidine formed a stable adduct with BF_3, while failed to form adducts with BMe_3 (Scheme 1.1).[2] They contributed this result to the steric conflict of the methyl groups of lutidine and BMe_3 after examining the molecular models.



Scheme 1.1

In 1950, Wittig described that Ph_3CNa reacting with $THF{\cdot}BPh_3$ resulted not in the displacement of THF by the trityl anion, but rather the trityl anion effected the opening of the THF ring affording the anion $[Ph_3C(CH_2)_4OBPh_3]^-$ (Scheme 1.2).[3] And later on, Damico and Broaddus discovered that when the trityl cation encountered with sterically encumbered amines affording an iminium cation, instead of undergoing amine-quaternization (Scheme 1.2).[4] Though all the bulkiness of the Lewis pairs was realized, which precluded the formation of classical Lewis acid/base adducts, the potential impact on subsequent reactivity was not pursued.



Scheme 1.2

It is until Stephan's group, who in exploring the olefin polymerization catalysts, queried the impact of steric bulk in Lewis' principle. The sterically hindered Lewis donors and acceptors preclude the formation of Lewis acid-base adducts which was later termed as Frustrated Lewis Pairs (FLPs), because of their "unquenched" reactivity, such systems are very reactive and are able to activate small molecules facilely.[5-8] This concept of FLPs has been extended to demonstrate new reactivity, ultimately leading to new approaches in catalysis.

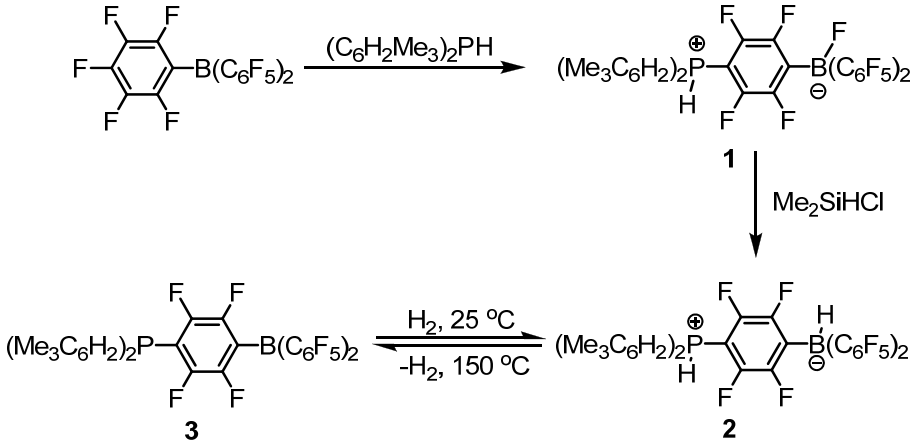
1. H_2 Activation by Frustrated Lewis Pairs

1.1 Phosphorus/Boron system in H_2 Activation

1.1.1 $(C_6H_2Me_3)_2P(H)(C_6F_4)B(H)(C_6F_5)_2$: Reversible H_2 Activation

Stephan and his co-workers unveiled the concept of Frustrated Lewis Pairs (FLPs), in which Lewis acids and bases are combined where the Lewis acidity and basicity remain

unquenched because of the steric conflict. But such "unquenched" acidity and basicity are quite reactive toward other molecules. In 2006, they discovered that the sterically demanding secondary phosphine $(C_6H_2Me_3)_2PH$ reacted with $B(C_6F_5)_3$ to effect the *para*-nucleophilic aromatic substitution, affording the zwitterionic compound $[(C_6H_2Me_3)_2P(H)(C_6F_4)B(F)(C_6F_5)_2]$ **1** (Scheme 1.3),[5] which was subsequently treated with Me_2SiHCl to yield $[(C_6H_2Me_3)_2P(H)(C_6F_4)B(H)(C_6F_5)_2]$ **2** (Scheme 1.3). In toluene solution,

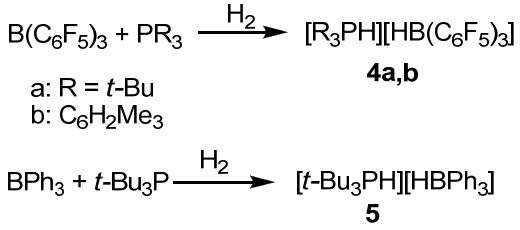


Scheme 1.3

compound **2** underwent stiochiometric loss of H_2 when the temperature reached 150 °C yielding phosphinoborane species $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ **3** (Scheme 1.3). The loss of H_2 was also confirmed by a dramatic color change from colorless to orange-red (λ_{max}: 455 nm; ε = 487 liters cm^{-1} mol^{-1}). This red-orange color was attributed to an internal charge transfer from the weak π-donation of the P atom to electron accepting of the B atom, which has been proposed for the related acetylene-based phosphinoborane $Ph_2PC{\equiv}CB(C_6H_2Me_3)_2$.[9-10] Remarkably, the isolated compound **3** reacted with H_2 at 25 °C proceeded smoothly with rapid loss of the orange color to give the colorless solution of **2**. This outstanding founding demonstrates that reversible small-molecule activation is achievable in the absence of a transition metal center. In addition, although this system reversibly binds less than 0.25 weight % of H_2, it does suggest that new strategies for chemical hydrogen storage may involve Lewis acid-Lewis base cooperative reactivity.

1.1.2 Heterolytic Activation of H_2 by Intermolecular Phosphine–Borane systems

In order to gain insight into the generality of this heterolytic H_2 activation by Frustrated Lewis Pairs, simply sterically encumbered phosphines R_3P (R = *t*-Bu, 2,4,6-$C_6H_2Me_3$) with $B(C_6F_5)_3$ were combined.[11] No evidence showed these mixtures to undergo the "neutralization" reaction at 25 °C or upon cooling to -50 °C. Exposure of these phosphine/borane mixtures to an atmosphere of H_2 at 1 atm pressure and 25 °C resulted in heterolytic cleavage of H_2 affording the phosphonium borates **4a** and **4b** (Scheme 1.4). A crystallographic study revealed that the *BH* and *PH* units in the anion and the cation are oriented toward each other with the BH···HP separation of 2.75 Å (Figure 1.1), which is much larger than typical intermolecular hydrogen bonding. Despite this orientation in the solid state, heating of this species to 150 °C did not lead to the loss of H_2.



Scheme 1.4

Several other phosphine/borane combinations were also investigated in order to probe the range of Lewis acidity and basicity required for this facile heterolytic activation of H_2. Reaction of tBu$_3$P and BPh_3 with H_2 slowly gave the salt [tBu$_3$PH][$HBPh_3$] **5** in 33% yield (Scheme 1.4). The longer reaction time in this case presumably due to the reduced Lewis acidity at boron. The analogous combination of $(C_6H_2Me_3)_3P$ and BPh_3, $(C_6F_5)_3P$ and $B(C_6F_5)_3$, or *t*-Bu_3P and $B(C_6H_2Me_3)_3$ resulted in no reaction at 25 °C under an atmosphere of H_2. These results support the view that reaction with H_2 takes place only under favorable electronic conditions. The Lewis acidity/basicity must be correctly matched in terms of cumulative strength to effect heterolytic cleavage of H_2.

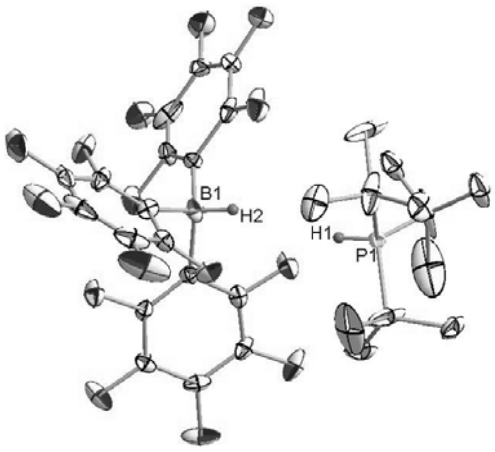


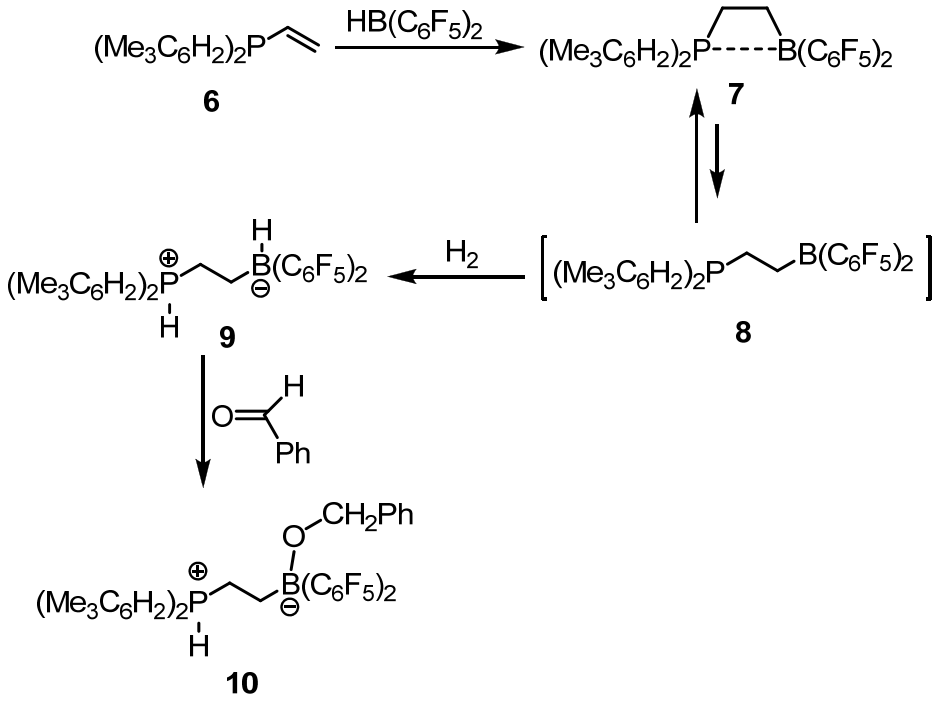
Figure 1.1 Molecular structure of compound ***4a***

1.1.3 Heterolytic Activation of H_2 by Intramolecular FLP $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$

The Erker group extended such activation of H_2 by the FLP to alkyl-linked phosphino-borane.[12] They first prepared the four-membered cyclic intramolecular phosphane-borane adduct **7** (Scheme 1.5), in which the B-P distance was 2.21 Å based on the calculated results. The parallel arrangement of one P-mesityl ring with one B-C_6F_5 group leads to π-π donor-acceptor interaction between these spatially close aryl π-systems, which stabilized the unusual four-membered heterocyclic structure. The DFT calculation localizes two isomeric open chain local minima of **7** (*gauche*-**8**, *trans*-**8**), which are both only ca. 7 kcal mol^{-1} above the cyclic ground state of **7** (Scheme 1.5).

Exposure of a solution of **7** to an atmosphere of H_2 (1.5 bar) at room temperature immediately produced a large amount of white precipitation, which was subsequently identified as the inner phosphonium-borate salt $(C_6H_2Me_3)_2PH^+CH_2CH_2BH^-(C_6F_5)_2$ **9** (Scheme 1.5). The borohydride moiety in **9** rapidly transfers the hydride anion to the carbonyl carbon of a phenylaldehyde, with the formation of the respective zwitterionic product $(C_6H_2Me_3)_2PH^+CH_2CH_2B^-(OCH_2Ph)(C_6F_5)_2$ **10** (Scheme 1.5).

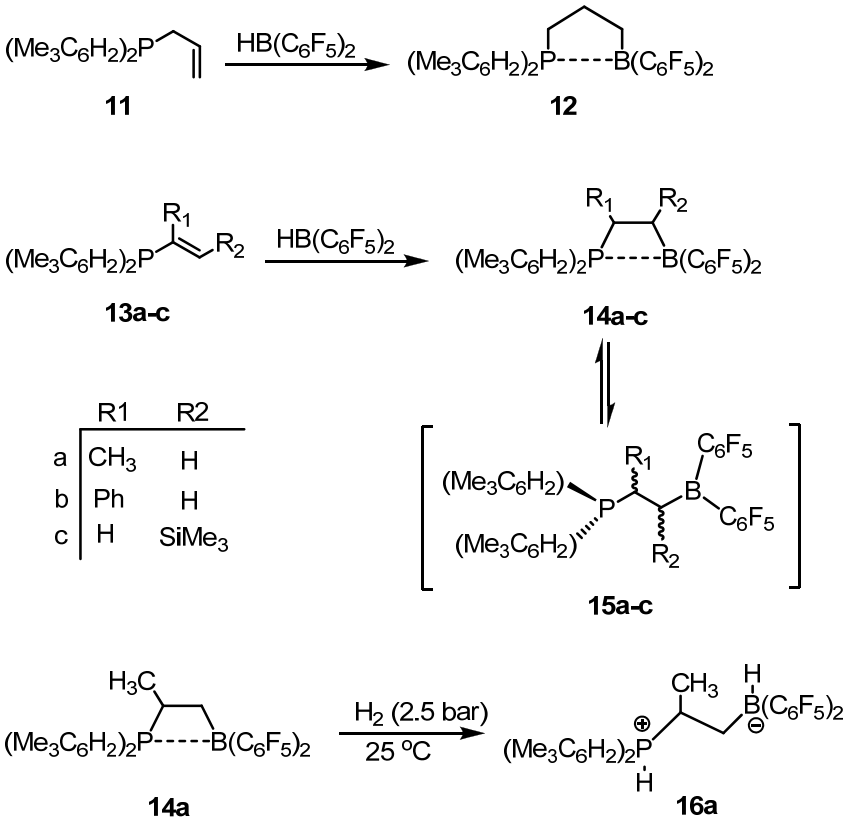
After that, they prepared several other intramolecular cyclic phosphane-borane adducts by incorporation of substituents in the alkyl-chain linking boron and phosphorus (Scheme 1.6) and obtained some experimental evidence regarding the thermal ring-opening.[13] Compound **12** was characterized by an X-ray crystal structure analysis, which revealed that three carbon



Scheme 1.5

atoms, the phosphorus and the boron center make up a core of the molecule that features a slightly distorted cyclopentane-like envelope conformation. The B-P bond length is 2.092(7) Å, which is slightly longer as compared to the related reference compounds $[PhP(CH_2)_3B(C_6F_5)_2]$ (2.062(2) Å) or $[Ph_2P(CH_2)_4B(C_6F_5)_2]$ (2.021(2) Å).[14-16] But the equilibrium between the open-chain and five-membered donor-acceptor forms was not observed in this case. Compounds **14a-c,** however, underwent rapid equilibration of open isomer and the cyclic form. The activation energy of the reversible P···B cleavage of these substrates were determined by dynamic ^{19}F NMR spectroscopy (**14a**: $\Delta G^{\#}_{inv}$ (280K) = 11.7 ± 0.4 kcal mol^{-1}). Compound **14b** and **14c** showed similar B-P dissociation values.

Whereas no evidence could be provided that compound **12**, **14b** and **14c** enable heterolytic activation H_2 under typical reaction condition (i.e. ambient temperature, at 2.5 bar or 60 bar H_2 pressure). Only compound **14a** reacted with H_2 to give the zwitterionic product **16a**. This indicates that the P···B bond cleavage seems not to be a limiting factor for H_2 activation, however, the steric interactions may play a significant role.

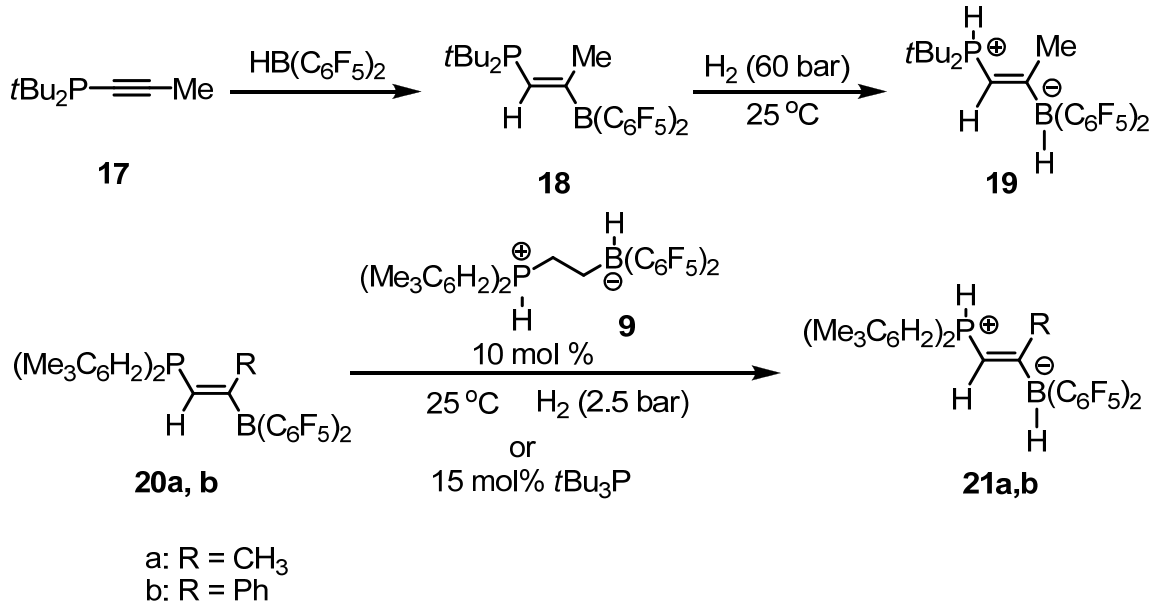


Scheme 1.6

1.1.4 Other Phosphorus/Boron systems in H_2 Activation

1.1.4.1 Alkenylene-Linked FLP in H_2 Activation

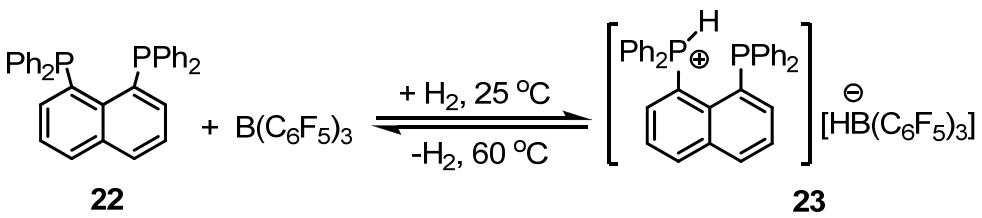
Hydroboration of tBu$_2$PC≡CCH$_3$ with HB(C$_6$F$_5$)$_2$ at 80 °C in benzene solution gave the bifunctional phosphane/borane compound tBu$_2$PCH=C(CH$_3$)B(C$_6$F$_5$)$_2$ **18** (Scheme 1.7), which reacted slowly with H_2 at elevated pressure (60 bar H_2, 3 h at room temperature) to yield the zwitterionic product **19**.[17] In contrast to compound **18**, neither compound (Me$_3$C$_6$H$_2$)$_2$PCH=C(CH$_3$)B(C$_6$F$_5$)$_2$ **20a** nor (Me$_3$C$_6$H$_2$)$_2$PCH=C(Ph)B(C$_6$F$_5$)$_2$ **20b** reacted with H_2 under the typical condition of 2.5 bar H_2 at room temperature, nor with H_2 at a pressure of 60 bar. However, addition of 15 mol% of tBu$_3$P to a toluene solution of **20a** led to a complete conversion into **21a** within 3h at room temperature under the elevated H_2 pressure (60 bar) (Scheme 1.7). Alternatively, compound **20a** could accept the H^+/H^- pair from (C$_6$H$_2$Me$_3$)$_2$PH$^+$CH$_2$CH$_2$BH$^-$(C$_6$F$_5$)$_2$ **9** to form the corresponding salt **21a** (Scheme 1.7).



Scheme 1.7

1.1.4.2 1,8-Bis(diphenylphosphino)naphthalene/B(C_6F_5)$_3$ in H_2 Activation

The Erker group also developed a new sterically hindered double Lewis base 1,8-bis(diphenylphosphino)-naphthalene **22** (Scheme 1.8), which is capable of activating H_2 heterolytically together with $B(C_6F_5)_3$ to yield the phosphonium hydridoborate salt **23** (Scheme 1.8).[18] The single-crystal X-ray diffraction analysis revealed that the phosphonium cation and the hydridoborate anion featured a rather close PH···HB contact of 2.08 Å (Figure 1.2). Heating a solution of the salt **23** in benzene solution resulted in a quantitative formation of **22** and $B(C_6F_5)_3$. This system is the rare examples of an observed reversible activate H_2 at Frustrated Lewis Pair chemistry.



Scheme 1.8

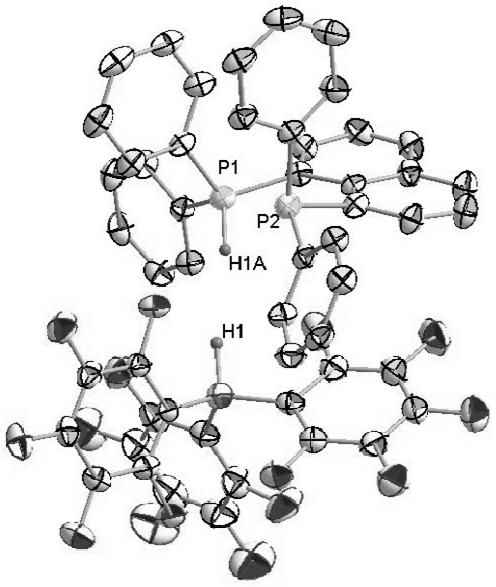


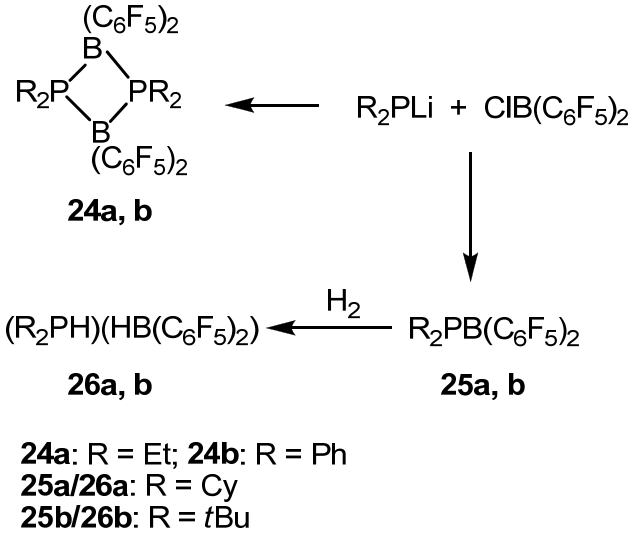
Figure 1.2 Molecular structure of compound ***23***

1.1.4.3 Phosphidoboranes $R_2PB(C_6F_5)_2$ in H_2 Activation

The computational study by Manners and co-workers suggested that the combination of electron-donating and electron-withdrawing groups on N and B, respectively, would afford amino-boranes capable of reacting with H_2.[19] In order to apply the "Frustrated Lewis Pairs" specifically to amino-boranes, Stephan's group prepared related phosphinoboranes from the reaction of secondary lithium phosphides (R_2PLi, R = Et, Ph, Cy, *t*Bu) with $(C_6F_5)_2BCl$.[20] The results showed that sterically undemanding substituents on phosphorus gave the dimeric products **24a, b** (Scheme 1.9), which exhibited inactivity toward H_2 (4 atm) over a period of 4 weeks. Sterically demanding groups, however, resulted in the formation of the monomeric species, **25a, b**, which retained the donor and acceptor properties at phosphorus and boron, respectively. In contrast to the dimeric products **24a, b**, the monomeric compound **25a, b** underwent slow reaction with H_2 at 60 ^oC affording the phosphine-borane adduct **26a, b** in 48 h.

DFT studies of H_2 activation by phosphinoborane **25b** showed that H_2 initially attacks the Lewis acidic boron, using the H-H bond as a Lewis base (H_2 complex). Thereafter, the coordinated H_2 rotates so that its bond lies parallel to the B-P bond, whereupon the H-H bond

is split with formation of the new H-P bond. Coordination of the H_2 molecule to the boron center represents the activation barrier of 22 kcal mol^{-1} for the process. Subsequent steps are essentially barrierless. The exothermicity of the process (-43 kcal mol^{-1}) presumably accounts for the irreversibility of the reaction.

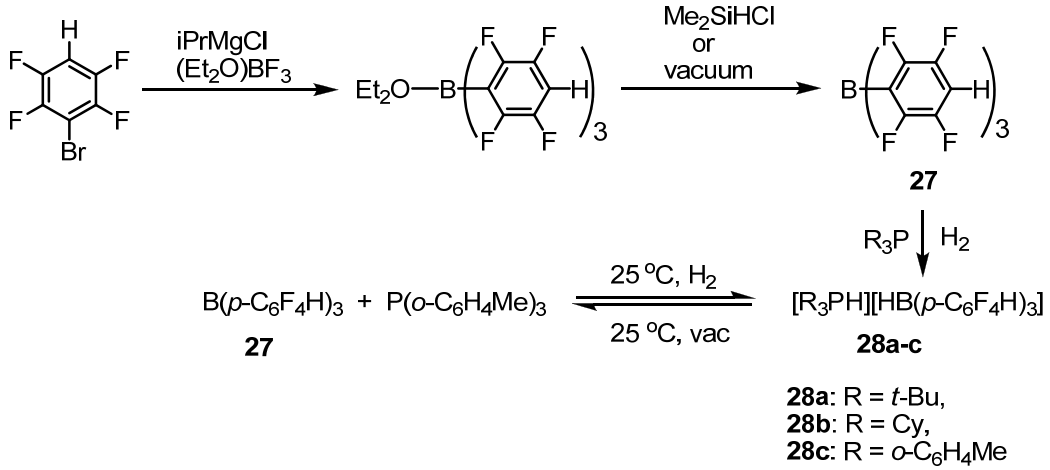


Scheme 1.9

1.1.4.4 FLPs with B(p-$C_6F_4H)_3$ in the H_2 Activation process

Following the pioneering work of Stephan's group, an increasing number of new FLPs capable of heterolytic activation of H_2 were then beginning to appear in the literature. But the FLP system capable of facile and reversible H_2 activation are rare, only the initial arene-linked system and subsequently the bis(phosphino)naphthalene/$B(C_6F_5)_3$ system are known to take up H_2 at 25 ^oC and release it under thermal treatment. The metal-free H_2 activation by simple combination of sterically encumbered phoshines R_3P (R = *t*-Bu, 2,4,6-$C_6H_2Me_3$) and $B(C_6F_5)_3$ is remarkable. None of the resulting salts could liberate H_2 again even at high temperature. This inability was attributed to an inappropriately strong Lewis basicity of the R_3P and Lewis acidity of the $B(C_6F_5)_3$ fragments, respectively. Thus, modification of the boron partner of the pairs was considered. Thus early studies implied that a strong Lewis acidic system was required. And in order to preclude the nucleophilic aromatic

substitution at *para*-position of a C_6F_5 ring on $B(C_6F_5)_3$ by the phosphine, the Stephan group targeted the preparation of the yet unknown borane $B(p\text{-}C_6F_4H)_3$ **27** (Scheme 1.10).[21] Its synthesis was accomplished by treatment of $BF_3(OEt_2)$ with the appropriate Grignard reagent. The pure product was obtained by sublimation *in vacuo* at 120 °C. Employing the Gutmann-Beckett and Childs methods,[22-26] compound **27** was shown to exhibit about 5 % less Lewis acidity in comparison with $B(C_6F_5)_3$.



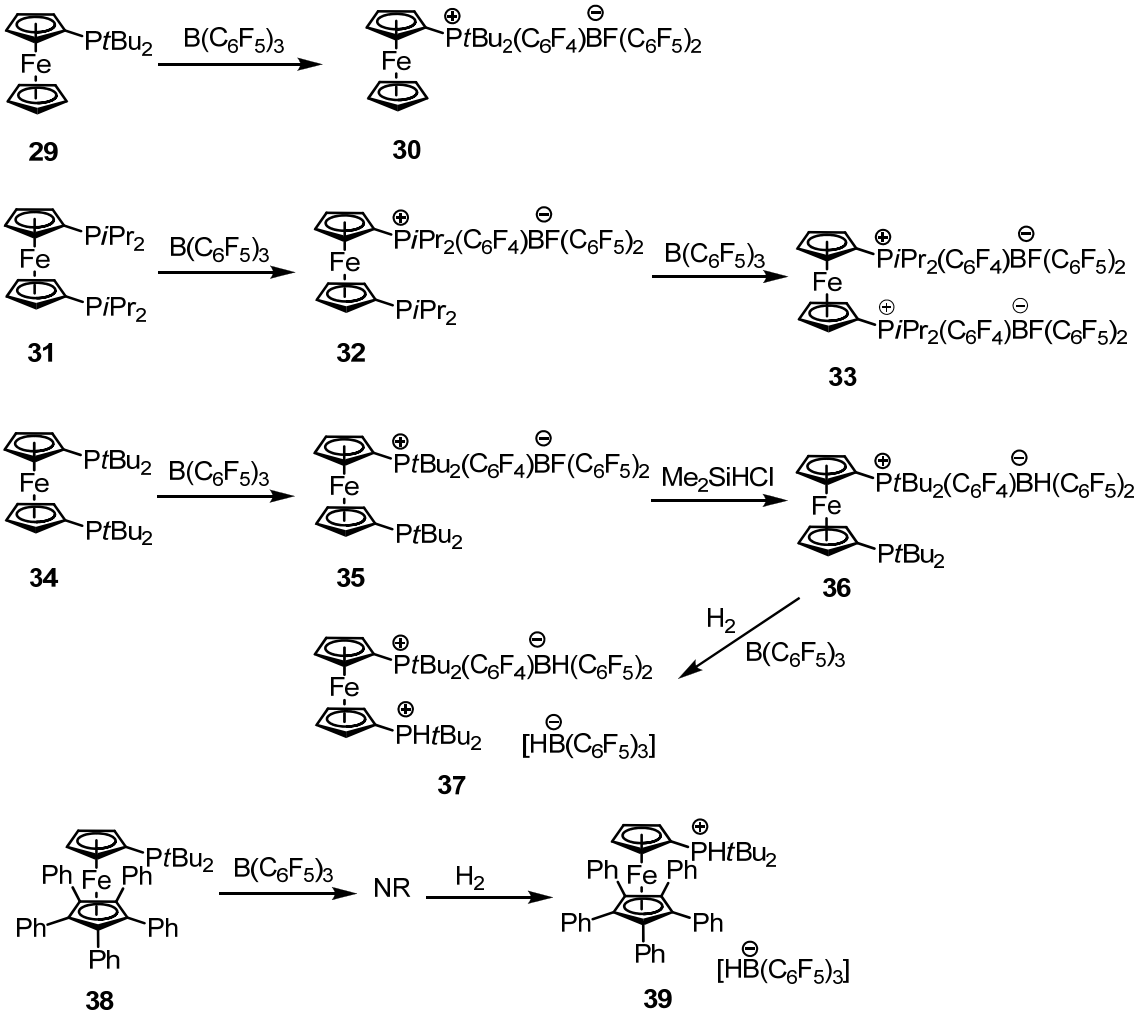
Scheme 1.10

Treatment of $B(p\text{-}C_6F_4H)_3$ **27** with PR_3 (R = *t*Bu, Cy, *o*-C_6H_4Me) under an atmosphere of H_2 at 25 °C rapidly produced the corresponding phosphonium hydridoborates **28a-c** (Scheme 1.10). Further investigation demonstrated that product $[(o\text{-}C_6H_4Me)_3PH][HB(p\text{-}C_6F_4H)_3]$ **28c** underwent slow liberation of H_2 under static vacuum at 25 °C, but this process would be accelerated when heated to 80 °C under vacuum, yielding 85 % of free phosphine and borane within 12 h. In contrast, products **28a**, **b** showed no signal of H_2 liberation under the same condition.

1.1.4.5 Phosphinometallocene-Based FLPs in H_2 Activation

Mono- and bis-phosphinoferrocenes as sterically demanding Lewis bases have also been applied in FLPs together with $B(C_6F_5)_3$ activating H_2.[27] The reaction of the

phosphinoferrocene $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4P\textit{t}Bu_2)]$ **29** with $B(C_6F_5)_3$ gave the product $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4P\textit{t}Bu_2(C_6F_4)BF(C_6F_5)_2)]$ **30** (Scheme 1.11), in which the phosphinoferrocene attacks at the *para*-carbon of a C_6F_5 ring prompting fluoride transfer to B. This nucleophilic attack is presumably a result of steric bulk that precludes the formation of Lewis acid-base adducts. The 1:1 stoichiometric reaction of the bis-phosphinoferrocene $[(\eta^5\text{-}C_5H_4PR_2)_2Fe]$ (R = *t*Bu, *i*Pr) and $B(C_6F_5)_3$ resulted in the mono-*para*-substitution

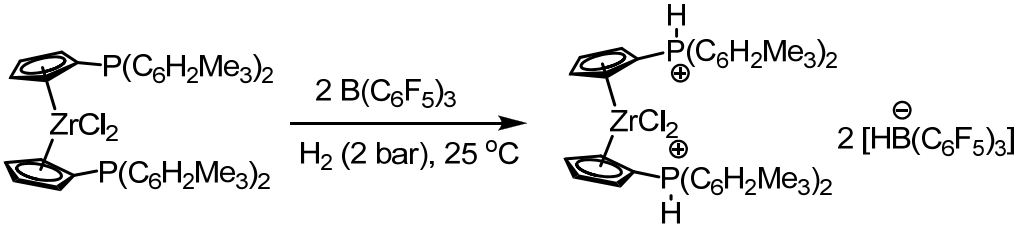


Scheme 1.11

products in the form of $[(\eta^5\text{-}C_5H_4P\textit{t}Bu_2)Fe(\eta^5\text{-}C_5H_4P\textit{t}Bu_2(C_6F_4)BF(C_6F_5)_2)]$ **35**, $[(\eta^5\text{-}C_5H_4P\textit{i}Pr_2)Fe(\eta^5\text{-}C_5H_4P\textit{i}Pr_2(C_6F_4)BF(C_6F_5)_2)]$ **32** (Scheme 1.11). Addition of second equivalent of $B(C_6F_5)_3$ to a BrC_6H_5 solution of compound **32** resulted in the formation of a

new species [(η^5-$C_5H_4PiPr_2(C_6F_4)BF(C_6F_5)_2$)Fe($\eta^5$-$C_5H_4PiPr_2(C_6F_4)BF(C_6F_5)_2$)] **33** (Scheme 1.11). But no further reaction could be observed between the product **35** with the second equivalent of $B(C_6F_5)_3$. The contrasting reactivities of **32** and **35** with additional $B(C_6F_5)_3$ suggested that the increased steric congestion of **35** precluded further reaction with $B(C_6F_5)_3$. Subsequent reaction of **35** with Me_2SiHCl afforded [(η^5-$C_5H_4PtBu_2$)Fe(η^5-$C_5H_4PtBu_2(C_6F_4)BH(C_6F_5)_2$)] **36**, which became ready to activate H_2 heterolytically in the presence of $B(C_6F_5)_3$ yielding [(η^5-$C_5H_4PHtBu_2$) Fe(η^5-$C_5H_4PtBu_2(C_6F_4)BH(C_6F_5)_2$)][$HB(C_6F_5)_3$] **37** (Scheme 1.11). It is obvious that the remaining P center of **36** is sterically encumbered enough to preclude interaction with $B(C_6F_5)_3$ and this unquenched Lewis basicity and acidity prompts the activation of H_2. Reaction of similar sterically encumbered ferrocenylphosphines [(η^5-C_5Ph_5)Fe(η^5-$C_5H_4PtBu_2$)] with $B(C_6F_5)_3$ showed the formation of a FLP. Exposure of this mixture to H_2 resulted in the immediately formation of [(η^5-C_5Ph_5)Fe(η^5-$C_5H_4PHtBu_2$)][$HB(C_6F_5)_3$] **39** (Scheme 1.11) in a high yield.

A related early transition metal metallocene derivative has been shown to exhibit similar frustrated Lewis pair with $B(C_6F_5)_3$ to activate H_2 heterolytically under mild condition to produce the salt **41** (Scheme 1.12).[28]



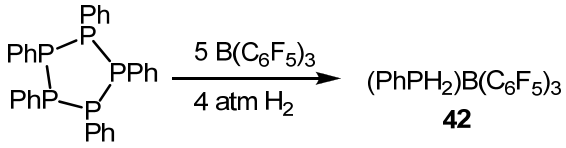
40 **41**

Scheme 1.12

1.1.4.6 P_5Ph_5 /$B(C_6F_5)_3$ in H_2 Activation

Combination of the cyclic P_5Ph_5 and $B(C_6F_5)_3$ produces a Frustrated Lewis Pair, that can activate H_2 to yield the phosphine adduct $(PhPH_2)B(C_6F_5)_3$ **42** (Scheme 1.13).[29] This

hydrogenation reaction is thought to proceed via initial heterolytic cleavage of H_2 by $P_5Ph_5/B(C_6F_5)_3$ to give $[P_5Ph_5H][HB(C_6F_5)_3]$. Subsequently, the borohydride counterion attacks on the transient phosphino-phosphinium to prompt the liberation of P_4Ph_4. As the P_4Ph_4 is not observed spectroscopically, the nature of the P-containing intermediates remains unclear. This FLP is also capable of activating secondary or tertiary silanes to yield $((R_3Si)PhPH)B(C_6F_5)_3$ and $((R_2SiH)PhPH)B(C_6F_5)_3$, respectively.

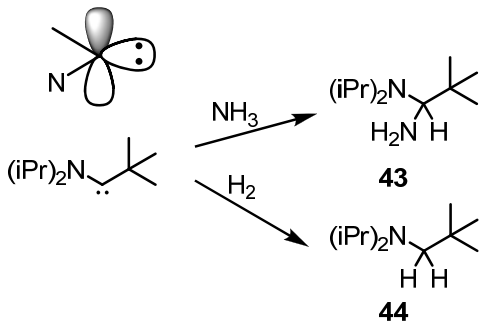


Scheme 1.13

1.2 Carbon/Boron and Nitrogen/Boron systems in H_2 Activation

1.2.1 Carbenes in FLP Activation of H_2

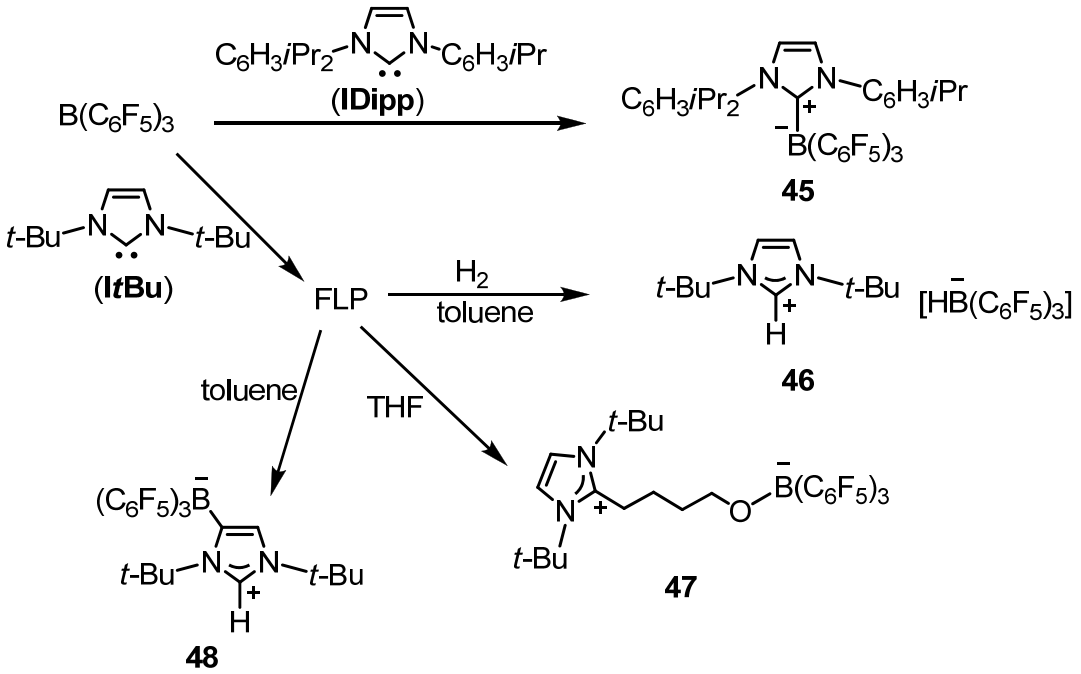
Following the initial report of the metal-free activation of H_2 by $[(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2]$ **2**, Bertrand and co-workers described that some carbene derivatives react both with H_2 and NH_3 to effect the heterolytic cleavage of H-H or N-H



Scheme 1.14

bonds (Scheme 1.14).[30] Indeed, these carbenes can be described as unique FLPs where the donor and acceptor site reside on the same atom and the orthogonal relationship of the lone pair and the vacant *p*-orbital results in unquenched Lewis acidity and basicity.

Subsequently, the Stephan and Tamm groups simultaneously applied the sterically hindered N-heterocyclic carbenes together with $B(C_6F_5)_3$ to the Frustrated Lewis Pairs chemistry.[31-32] Stephan group's initial effort found that the reaction of the NHC 1,3-bis(2,6-diisopropylphenyl)-1,3-imidazol-2-ylidene (IDipp) with $B(C_6F_5)_3$ forms stable, classical Lewis acid-base adduct (IDipp)$B(C_6F_5)_3$ **45** (Scheme 1.15). The combination of 1,3-di-*tert*-butylimidazolin-2-ylidene (I*t*Bu) with $B(C_6F_5)_3$, however, formed a carbene-borane FLP. The freshly generated FLP in H_2 atmosphere effected heterolytic cleavage of the H-H bond to produce [I*t*BuH][$HB(C_6F_5)_3$] **46** (Scheme 1.15). The X-ray diffraction analysis revealed that the C-H and B-H units in compound **46** are not oriented towards one another. Instead, the ions are found connected through multiple weak C-H···F hydrogen bonding interactions (Figure 1.3). This frustrated Lewis pair also effected the ring opening of THF giving [I*t*Bu$(CH_2)_4OB(C_6F_5)_3$] **47** (Scheme 1.15). But the limitations of this



Scheme 1.15

FLP, as Tamm et al. pointed out, was the instability in solution for a long time. The $B(C_6F_5)_3$ moiety attached to the 4-position of the imidazole heterocycle affording the product **48**, which

lost their reactivity towards H_2.

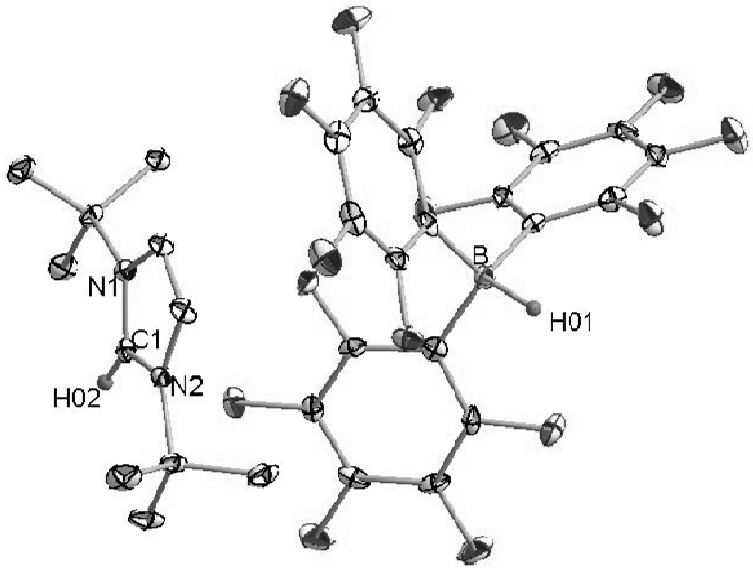
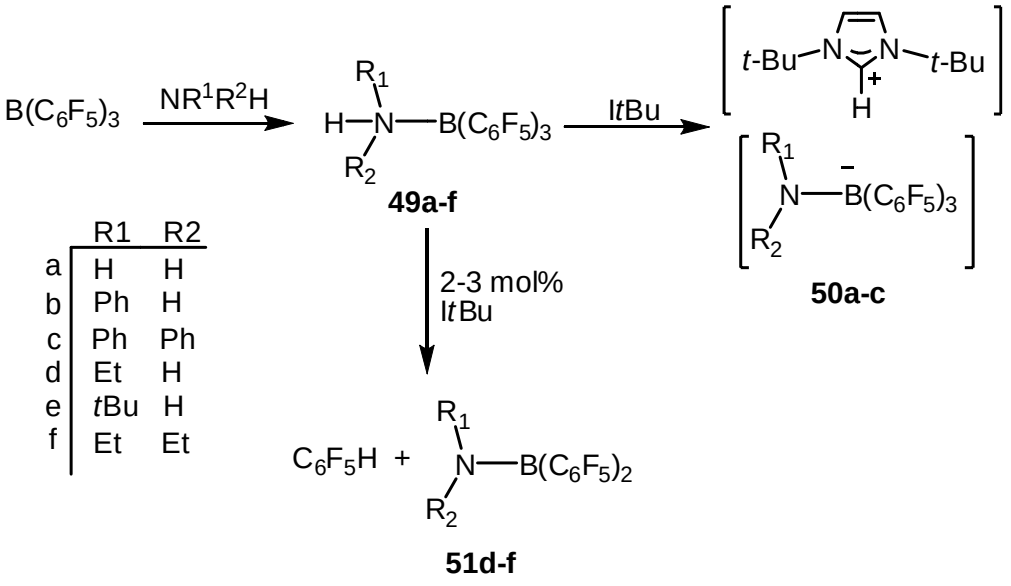


Figure 1.3 *Molecular structure of compound* ***46***



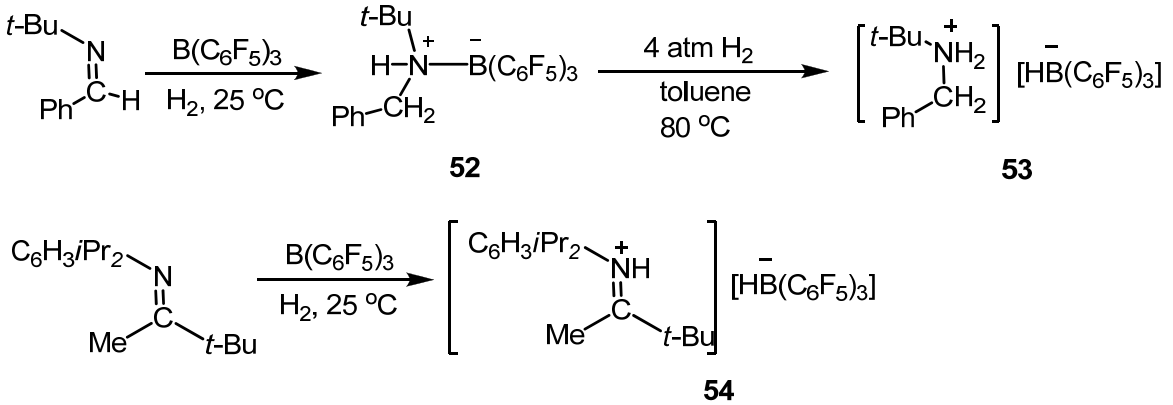
Scheme 1.16

In addition, the carbene I*t*Bu also reacted with ammonia, aniline, and diphenylamine adducts with $B(C_6F_5)_3$ to give new species **50a-c** (Scheme 1.16). The aniline, and diphenylamine adducts of $B(C_6F_5)_3$ were deprotonated by I*t*Bu generating ionic complexes **50a-c** is analogous to reaction with H_2. In contrast, reactions with the primary and secondary

alkyl amines, adducts with I*t*Bu resulted in the formation of the amino-boranes **51d-f** as well as C_6F_5H (Scheme 1.16). The presence and necessity of the carbene in the formation of **51d-f** suggests that these reactions are catalytic in the carbene, and indeed the reactions could be achieved in the presence of 2-3 mol% of I*t*Bu. The presumable mechanism of these reactions is that deprotonation of the initially formed amine adduct of $B(C_6F_5)_3$ by I*t*Bu affords an electron-rich aminoborate, then reacts with the transient imidazolium ion to eliminate C_6F_5H and regenerate carbene.

1.2.2 Imines and Amines in FLP Activation of H_2

The FLPs were not limited to boron-phosphorus system, they were extended to boron-carbene systems, but also to boron-imine or amine systems. Stephan's group has reported that the stoichiometric reaction between imine *t*BuN=C(H)Ph and $B(C_6F_5)_3$ with H_2 at room temperature gave the amine-borane adduct *t*Bu(PhCH$_2$)NH·$B(C_6F_5)_3$ **52** via reduction of the C=N bond (Scheme 1.17).[33] Heating the adduct at 80 °C for 1 h under H_2 (4 atm) prompted the dissociation of the B-N bond and subsequently split H_2 heterolytically to generate [*t*Bu(PhCH$_2$)NH$_2$][$HB(C_6F_5)_3$] **53** (Scheme 1.17). An X-ray crystal structure revealed that the refined NH_2 and BH hydrogen atoms display a B-H···H-N close contact of 1.87(3) Å (Figure 1.4).



Scheme 1.17

The analogous reaction of the ketimine DippN=CMe(*t*Bu) with $B(C_6F_5)_3$ under H_2 afforded the ion pair [DippN(H)=CMe(*t*Bu)][$HB(C_6F_5)_3$] **54** (Scheme 1.17). This result suggests that the steric bulk about the iminium cation precludes hydride transfer from the borate to the iminium carbon.

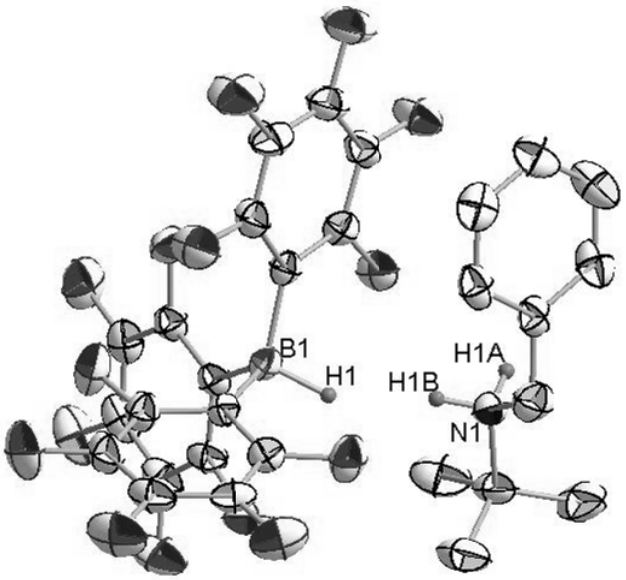
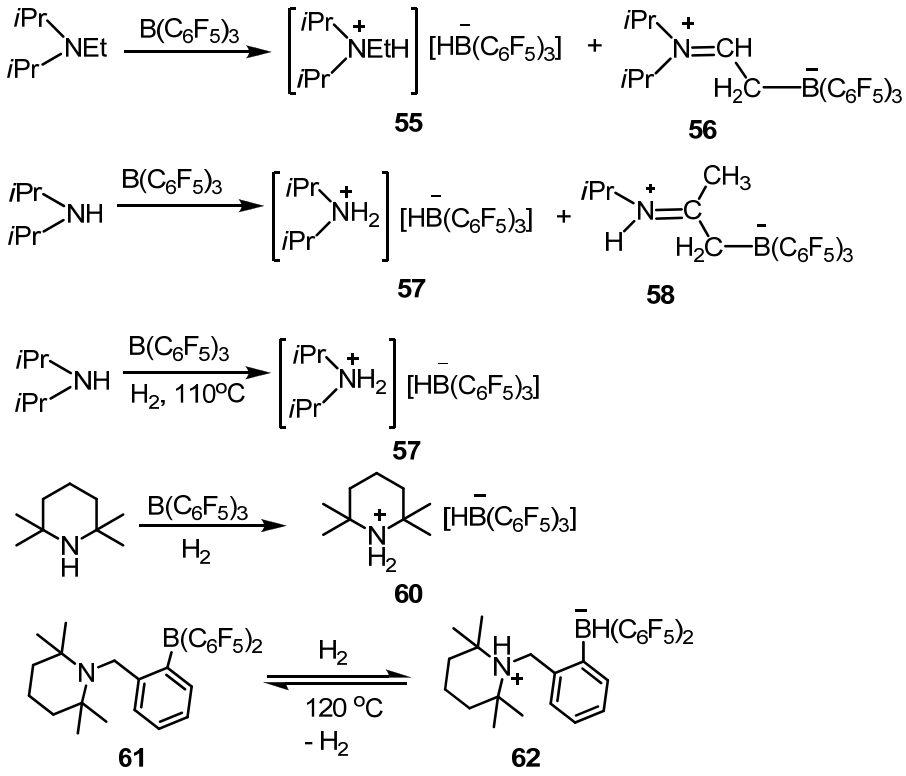


Figure 1.4 Molecular structure of compound ***53***

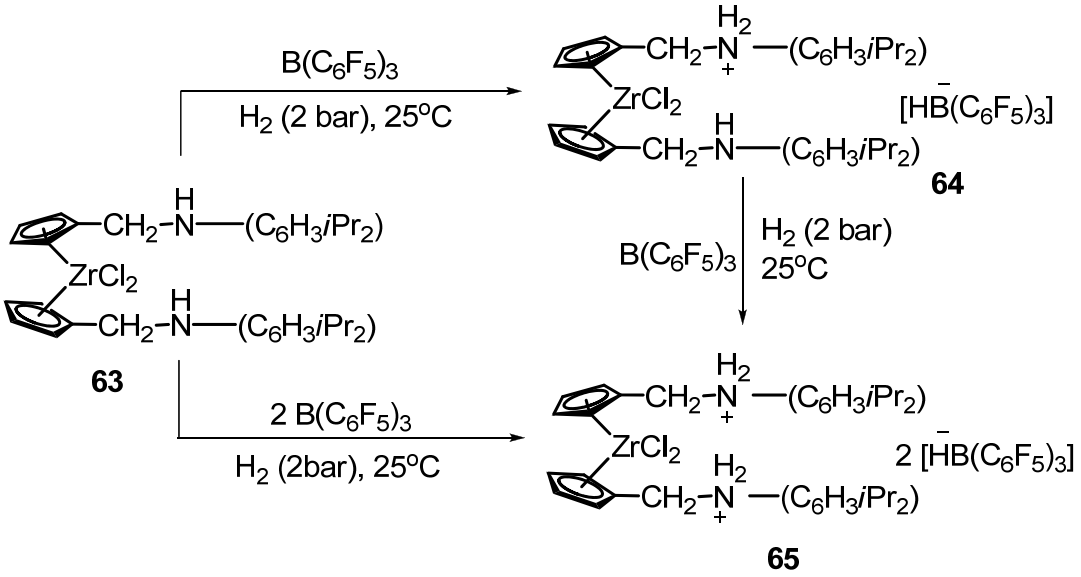
The Rieger and Repo groups extended FLP to amines/boron system. They discovered that the reactions of diisopropylethylamine and diisopropylamine with $B(C_6F_5)_3$ gave 1:1 mixtures of the salt **55** or **57** and the zwitterion **56** or **58** (Scheme 1.18).[34] But no reaction was observed between a bulky secondary amine 2,2,6,6-tetramethylpiperidine (**TMP**) and $B(C_6F_5)_3$. Whereas the reaction between diisopropylamine and $B(C_6F_5)_3$ is reversible at elevated temperature, so this system could split H_2 heterolytically at 110 ^oC to produce [*i*PrNH_2][$HB(C_6F_5)_3$] **57** in 95% (Scheme 1.18), but the same reaction could not occur by this system at room temperature. The FLP **TMP**···$B(C_6F_5)_3$, however, was capable of activation of H_2 facilely at room temperature to form the corresponding product [**TMP**H][$HB(C_6F_5)_3$] **60** (Scheme 1.18). Later, they prepared a linked amine-borane system (compound **61**, Scheme 1.18) capable of activating H_2 reversibly, which was then developed as an active catalyst to hydrogenate various imines.[35]



Scheme 1.18

1.2.3 Zirconocene Amines in FLP Activation of H_2

The Erker group reported that bis(arylimino-Cp)$ZrCl_2$ complex forms a "Frustrated" Lewis Pair with $B(C_6F_5)_3$, which rapidly reacts with H_2 (2 bar) at room temperature to give the organometallic monoammonium/hydridoborate **64** (Scheme 1.19), only if one molar equivalent of $B(C_6F_5)_3$ in the mixture.[36] Addition of a second equivalent of $B(C_6F_5)_3$ eventually afforded the zirconocene-bis(ammonium)/2[$HB(C_6F_5)_3$] **65** (Scheme 1.19). The salt **65** was proven an efficient catalyst for the hydrogenation of bulky imines and of silyl enol ethers.

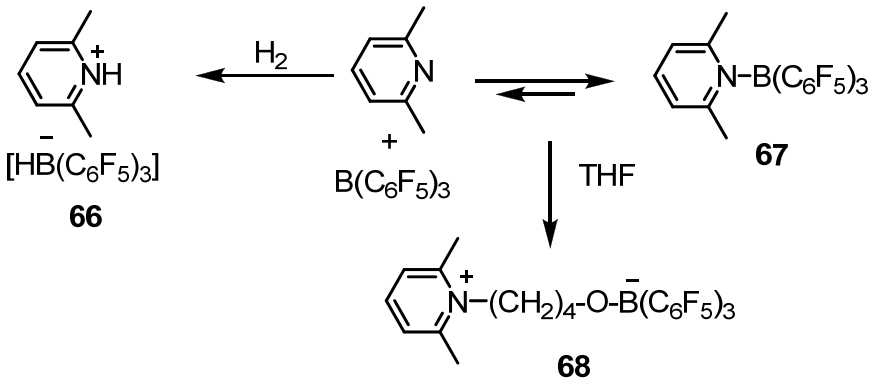


Scheme 1.19

1.2.4 Lutidine in FLP Activation of H_2

In 1942 Brown et al. reported the formation of pyridine adduct with BF_3 and BMe_3, the 2,6-lutidine was reported to be an exceptional case.[2] It was basic enough to form an adduct with BF_3, but it was too sterically encumbered to bind to BMe_3. While pyridine is known to form an adduct with $B(C_6F_5)_3$, the Stephan group were prompted to study the FLP case of Lutidine and $B(C_6F_5)_3$.[37] The result showed that the mixture of 2,6-lutidine and $B(C_6F_5)_3$ lead to an equilibrium between free lutidine/$B(C_6F_5)_3$ and the Lewis acid-base adduct $(2,6\text{-}Me_2C_5H_3N)B(C_6F_5)_3$ **67** (Scheme 1.20) based on the ^1H and ^{19}F NMR spectroscopy. Up cooling to -10 ^oC, the ^{19}F NMR resonances sharpen reflecting the presence of primarily a dissymmetric adduct $(2,6\text{-}Me_2C_5H_3N)B(C_6F_5)_3$ (Scheme 1.20). Determination of the equilibrium constants as function of temperature gave ΔH = -42(1) kJ/mol and ΔS = -131(5) J/mol·K. X-ray crystallographic analysis revealed a B-N bond length of 1.661(2) Å, significantly longer than that in $(py)B(C_6F_5)_3$ (1.628(2) Å).[38-39] The existence of an equilibrium between the adduct $(2,6\text{-}Me_2C_5H_3N)B(C_6F_5)_3$ and free lutidine/$B(C_6F_5)_3$ suggested the potential FLP reactivity. Addition of H_2 (1 atm, 2 h) to the mixture resulted in the pyridinium hydridoborate salt in 87% yield. This system could also effect ring opening of

THF yielding the zwitterionic salt **68** (Scheme 1.20).

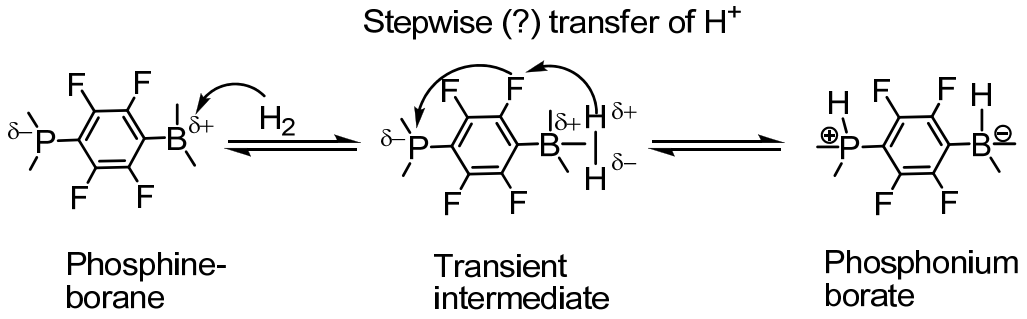


Scheme 1.20

2. Proposed Mechanism for the Activation of H_2 by Frustrated Lewis Pairs

2.1 Kubas' mechanism

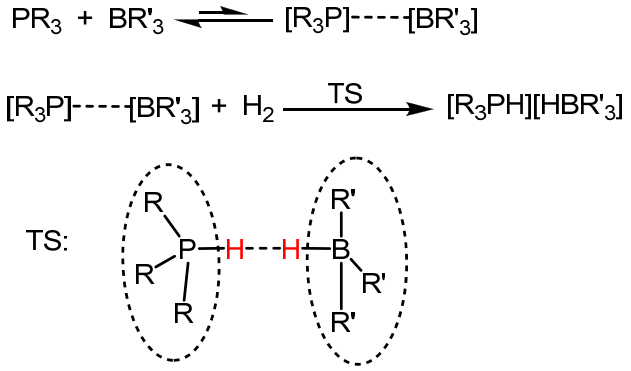
Since the discovery that H_2 splitting can be achieved by main group element Lewis acid–Lewis base pairs with steric hindrance which termed "Frustrated Lewis Pairs", a research for the mechanism for such kind of reaction was initiated. After the report by Stephan that reversible activation of H_2 could occur on metal-free center, Kubas proposed one mechanism for this reaction.[40] By analogy to transition-metal chemistry, it seemed that H_2 initially interacted with the electrophilic boron center, followed by proton migration from an H_2-like complex to the basic phosphorus atom, which is separated from the boron center by a perfluorophenyl linker (Scheme 1.21). This migration could proceed stepwise via the liker or could be assisted by the solvent. So a side-on interaction of H_2 and $B(C_6F_5)_3$ was assumed to initiate the dissociation process. Though early computational studies supported the existence of a weakly bound $H_3B\cdots H_2$ adduct, no evidence for the formation of the $H_2\cdots B(C_6F_5)_3$ was found in related experiments.



Scheme 1.21

2.2 Pápai 's mechanism

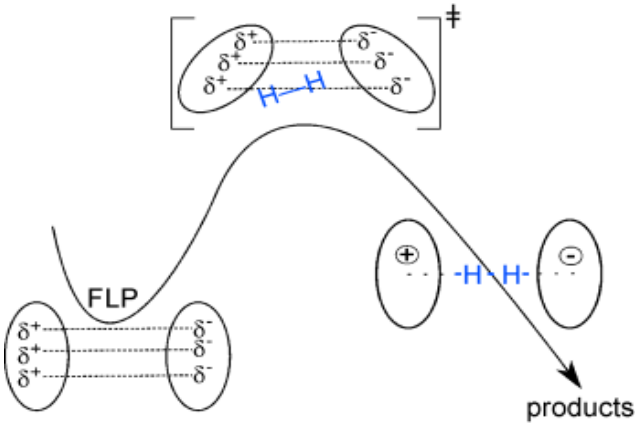
In order to gain further mechanistic insight into this reaction, Pápai initiated a theoretical study.[41-50] Their calculational result showed that there has been an appreciable delocalization of aryl π electrons into the *p* (B) orbital of $B(C_6F_5)_3$, which prevent the σ electrons of H_2 into boron vacant *p* orbital.[41] So the proposed intermediate of $(C_6F_5)_3B\cdots H_2$ actually was found to be quite unstable even at low temperature. As an alternative scenario, the end-on approach of H_2 to PR_3 was anticipated, because the previous low-temperature matrix-isolation work demonstrated that phosphines can interact with H_2 presumably via nucleophilic attack on the H_2 molecule in an end-on fashion. The calculational results also indicated that this interaction is repulsive. Based on the calculations and considering the ease of the activation of H_2 by FLPs, another novel mechanism for this kind of reaction (Scheme 1.22) was proposed. The new model involved the preorganization of loosely bound donor-acceptor encounter complexes, which are held together by multiple of CH···F hydrogen bonds. After that, the small molecule H_2 inserted into this flexible FLP to interact with both active centers to form an intermediate. The electron transfer occurs through simultaneous P----σ* (H_2) and σ (H_2)----$B(C_6F_5)_3$ donation in a push-pull matter and implies progressive weakening the H—H bond along the reaction pathway.[41]



Scheme 1.22

2.3 Grimme's mechanism

The latest computational studied by Grimme group casted some doubt on the linear P-H···H-B arrangement in the transition state proposed by Pápai.[51] Based on their calculations including dispersion forces, they presented an even simpler mechanistic picture to explain the H_2 activation by FLP. They pointed out that polarization of H_2 is induced by the electric field of the FLP inside its cavity (Scheme 1.23). The entrance of the H_2 into the FLP cavity is the key step of the reaction, once the H_2 inside the FLP cage, the reaction would proceed without a barrier. So the FLPs activate H_2 by polarization owing to the electric field created by their donor/acceptor atoms, and the observed reaction barriers are mainly due to the preparation step of the encounter complexes.



Scheme 1.23 Mechanism of H_2 activation by FLPs via encounter complex preparation and electrical field (dashed lines)

3. Metal-free Catalytic Hydrogenation

3.1 Catalytic hydrogenations by Phosphine/Borane FLPs

Catalytic hydrogenations of unsaturated organic compounds constitute an important class of chemical transformations and find broad applications both in chemical industry and laboratory organic synthesis. The majority of hydrogenation reactions involve the direct use of H_2 as the hydrogen source, and they are catalyzed by transition metals (TMs).[52-57] However, environmental and product toxicity concerns connected with TMs have long motivated investigations directed towards achieving TM-free homogeneous catalytic hydrogenation. KO*t*Bu has been shown to act as a catalyst effecting the addition of H_2 to benzophenone under forcing conditions of 200 ^oC and more than 100 bar H_2 pressure.[58] Organocatalysts have been developed for hydrogenations of enones and imines, however, such systems do not employ H_2 directly but rather a surrogate such as a Hantzsch ester as the stoichiometric source of hydrogen.[59-63] The development of non-metal hydrogenation catalysts depends on the discovery of systems that react cleanly with H_2, but few are known yet. Power and co-worekers reported the hydrogenation of Ge_2-alkyns analogues to give a mixture of Ge_2 and primary germane products.[64] However, a major breakthrough came only with very recently the discovery by Stephan and co-workers that a reversible TM-free H_2 addition/elimination process could be achieved by employing Frustrated Lewis Pairs. $[Mes_2P(C_6F_4)B(C_6F_5)_2]$ was shown to react readily with H_2 at very mild conditions, and its reduced form $[Mes_2P(H)(C_6F_4)B(H)(C_6F_5)_2]$ could release H_2 above 150^oC. This milestone experiment was then developed into catalysts for metal-free hydrogenations of imines, nitriles and aziridines (Table 1).[65]

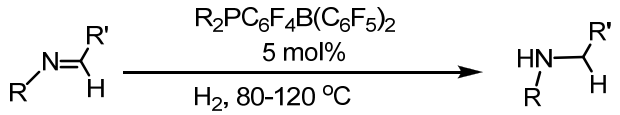
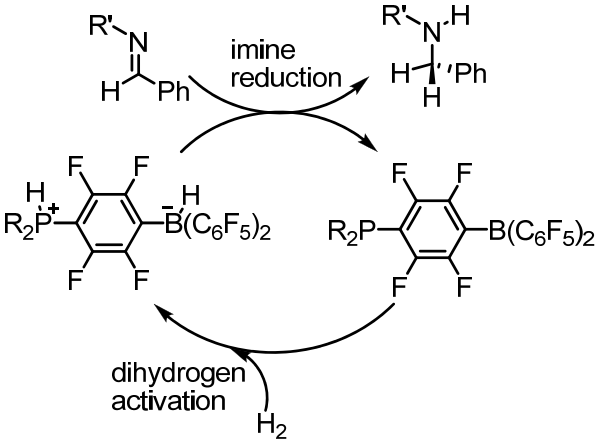


Table 1. Hydrogenation catalyzed by $Mes_2P(C_6F_4)B(C_6F_5)_2$ (1) and $tBu_2P(C_6F_4)B(C_6F_5)_2$ (2)

Entry	Substrate	Catalyst	T [°C]	t [h]	Yield [%]	Product
1	Ph(H)C=N*t*Bu	1[b]	80	1	79	$PhCH_2NHtBu$
2	Ph(H)C=N*t*Bu	2[b]	80	1	98	$PhCH_2NHtBu$
3	$Ph(H)C=NSO_2Ph$	1	120	10.5	97	$PhCH_2NHSO_2Ph$
4	$Ph(H)C=NSO_2Ph$	2	120	16	87	$PhCH_2NHSO_2Ph$
5	$Ph(H)C=NCHPh_2$	1	140	1	88	$PhPhCH_2NHCHPh_2$
6	$Ph(H)C=NCH_2Ph$	1	120	48	5[c]	$PhCH_2NHCH_2Ph$
7	$Ph(H)C=NCH_2Ph(B(C_6F_5)_3)$	1	120	46	57	$PhCH_2NHCH_2Ph(B(C_6F_5)_3)$
8	$MeCNB(C_6F_5)_3$	1	120	24	75	$MeCH_2NH_2B(C_6F_5)_3$
9	$PhCNB(C_6F_5)_3$	1	120	24	84	$PhCH_2NH_2B(C_6F_5)_3$
10	$(CH_2CH_2CNB(C_6F_5)_3)_2$	1[d]	120	48	99	$(CH_2CH_2CH_2NH_2B(C_6F_5)_3)_2$
11	PhCHCHPhNPh	1[d]	120	1.5	98	$PhCH_2CHPhNHPh$

[a] Standard conditions: 5 mol% catalyst, 4 mL toluene, ca. 5 atm H_2. [b] 1 atm H_2. [c] Determined by ^1H NMR spectroscopy. [d] 10 mol% catalyst.

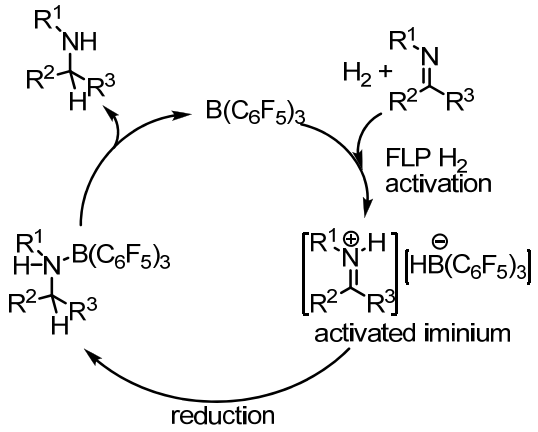


Scheme 1.24 Catalytic cycle for reduction of imines by $Mes_2P(C_6F_4)B(C_6F_5)_2$

A mechanism for this catalytic cycle was proposed following the idea that imines can initially be protonated by the phosphonium borate zwitterions to give an iminium salt, which then undergoes nucleophilic attack from the borohydride anion, transferring hydride and additionally affording the amine. Dissociation of the amine from the boron atom liberates the phosphine-borane, which then reacts with H_2 to regenerate the phosphonium borate (Scheme 1.24). An important aspect of the mechanism involves the suppression of the catalyst's

inhibition by amine-borane adduct formation. In some cases, amine dissociation can be prompted by the incorporation of sterically demanding substituents on the substrate that disfavor tight adduct formation. As well, elevated temperatures between 80-120 ^{o}C promote amine dissociation and speed up the catalytic reduction.

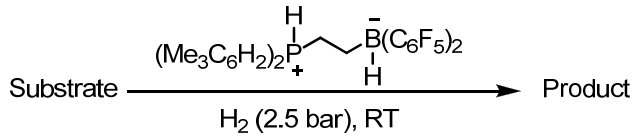
Later, Stephan and other group discovered that the Lewis acid $B(C_6F_5)_3$ itself is a good catalyst to reduce imines with H_2.[33] Simply combination of $B(C_6F_5)_3$ with sterically demanding aldimines and ketimines constitute FLPs that react with H_2, affording direct and catalytic reduction to amines. The first step of the catalytic cycle involves heterolytic H_2 splitting by the imine/borane FLP to generate an iminium hydridoborate ion pair. The hydride from the borohydride unit is then transferred to the iminium carbon (Scheme 1.25), after that dissociation of the B-N bond releases the product amine and regenerates the free borane to re-enter the cycle. The latter step of amine dissociation is thought to be the rate-determining step.

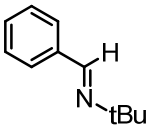
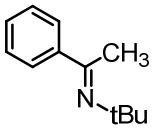
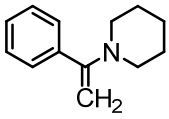
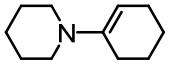
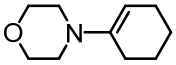
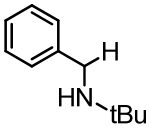
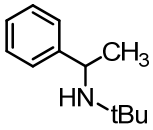
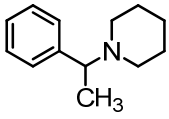
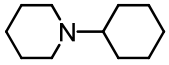
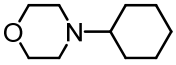


Scheme 1.25 Catalytic cycle for reduction of imines by $B(C_6F_5)_3$

In developing new FLP systems, the Erker group has published the four-membered cyclic phosphane/borane compound $(C_6H_2Me_3)P(CH_2CH_2)B(C_6F_5)_2$ which was shown to activate H_2 heterolytically in a facile manner. Interesingly, this reaction was not thermally reversible, but it was effective hydrogenation catalyst for reduction of imines and enamines at ambient temperature (Scheme 1.26).[17] For some substrate types, it is the most active metal-free

hydrogenation catalysts to date. Although in some cases, at least 20 mol% of catalyst is required, some other cases, 3 mol% of catalyst is sufficient to achieve near-complete enamine hydrogenation under mild conditions.



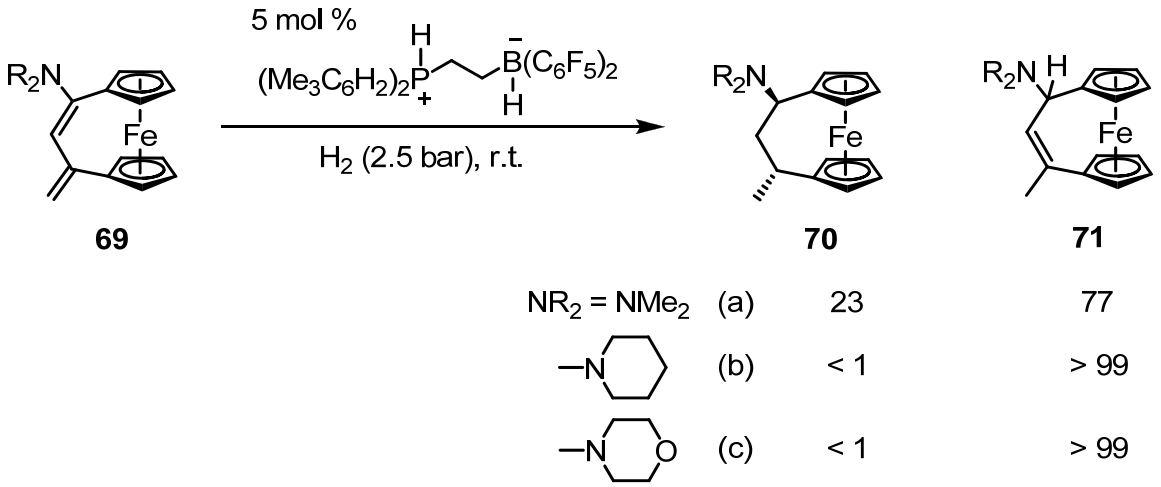
Substrate					
Product					
Catalyst (mol%)	20	5	10	5	3
Yield (%)	87	70	80	88	78

Scheme 1.26

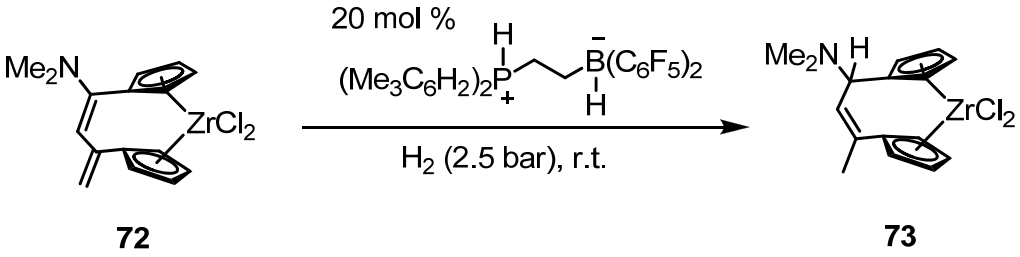
Treatment of compound **69** (-NR_2 = -NMe_2) with H_2 (2.5 bar) in the presence of 5 mol % of the catalyst $(C_6H_2Me_3)PH(CH_2CH_2)BH(C_6F_5)_2$ at room temperature resulted in the rapid formation of the hydrogenation products **71a** and **70a** in a 77:23 ratio (Scheme 1.27).[66] But when applied the more bulky dienamines (-NR_2 = -NC_5H_{10}, -NC_4H_8O) together with 5 mol% of the catalyst under H_2 atmosphere, the hydrogenation reactions are more selective. Only the 1,4-hydrogenation products are observed (Scheme 1.27).

The metal-free catalyst can be used for the selective hydrogenation of the conjugated dienamine moiety at the ansa-zirconocene compound **72** to produce the 1,4-hydrogenation product **73** (Scheme 1.28). The iminium-ion intermediate of this catalytic reaction was independently prepared by selective protonation of the dienamine **69a** with HCl, followed by anion exchange to give **74**-[BF_4]. This protonation process could also be achieved by treatment of **69a** with the organometallic ammonium/hydridoborate system

{[(CpCH$_2$NH$_2$Ar)$_2$ZrCl$_2$]$^{2+}$/2[HB(C$_6$F$_5$)$_3$]$^-$} giving **74**-[HB(C$_6$F$_5$)$_3$], which is stable at room

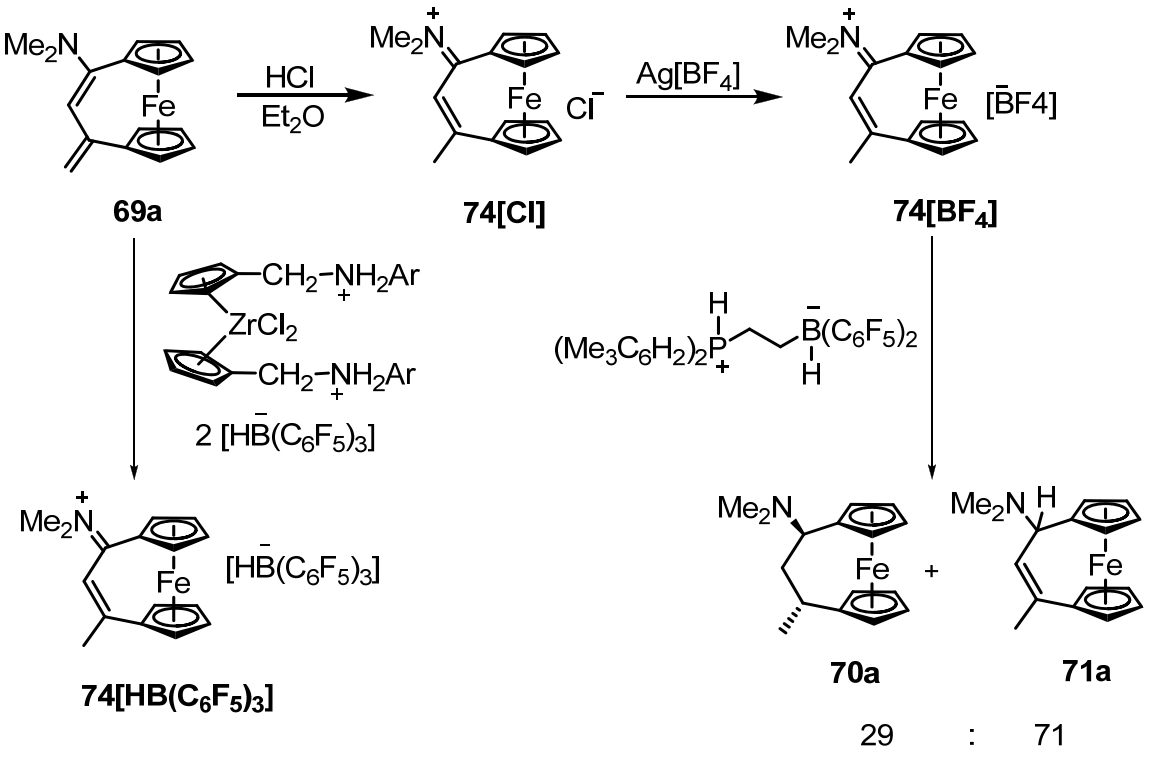


Scheme 1.27

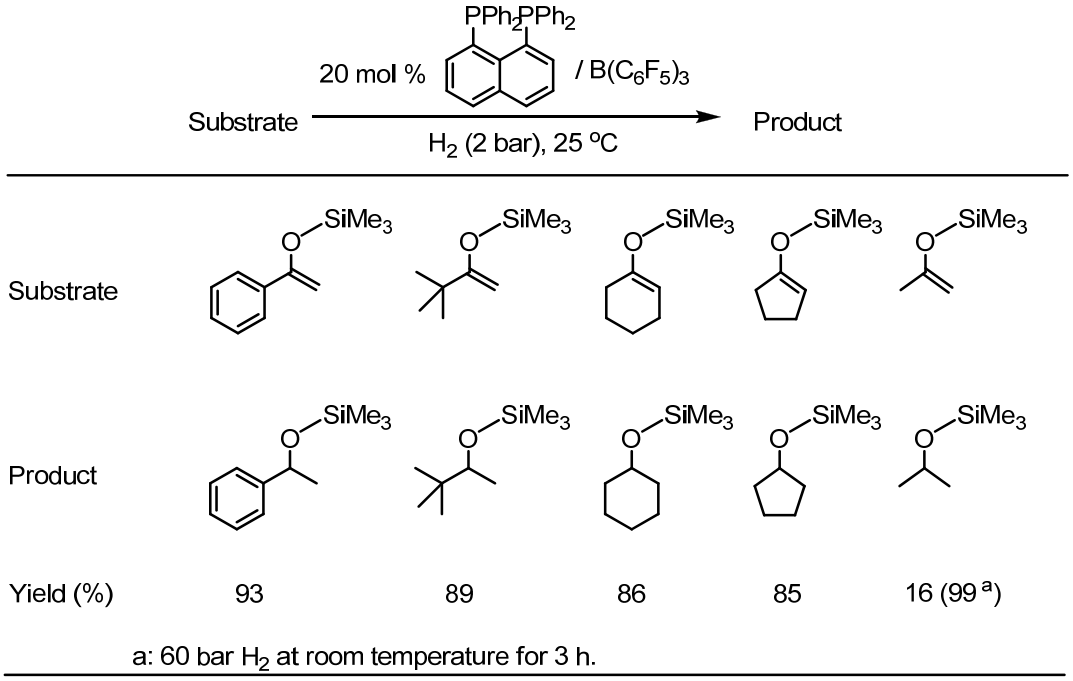


Scheme 1.28

temperature. Upon heating to 80 °C in C_6D_6, it is converted to a ca. 1:1 mixture of the product **70a** and **71a**. Treatment of the related **74**-[BF_4] salt with a stoichiometric amount of the compound ($C_6H_2Me_3$)PH(CH_2CH_2)BH(C_6F_5)$_2$ in C_6D_6 at 70 °C within 20 min resulted in the clean formation of the mixture **70a** and **71a** in a ratio of 29:71 (Scheme 1.29), which is quite similar to the ratio observed in the catalytic hydrogenation reaction. These experiments may indicate that the catalytic hydrogenation reaction initiated by proton transfer followed by hydride reduction of an in situ generated iminium ion intermediate.



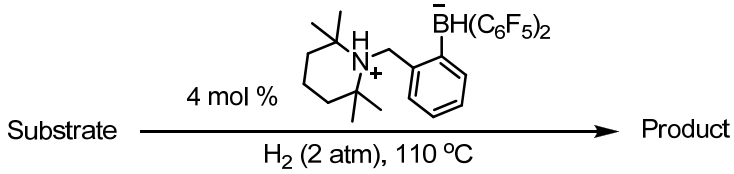
Scheme 1.29

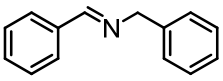
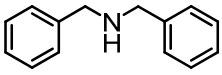
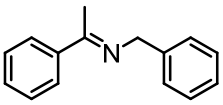
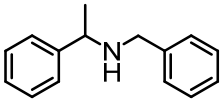
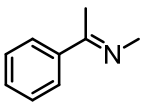
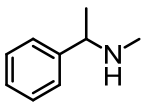
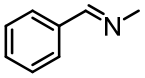
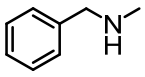
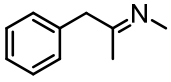
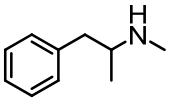
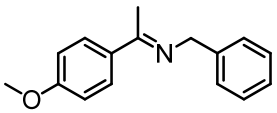
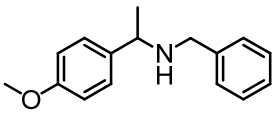
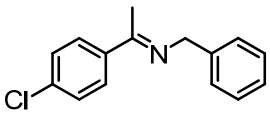
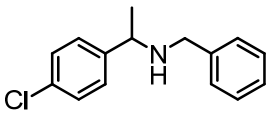
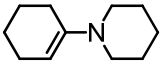
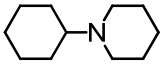


Scheme 1.30

The Erker group has developed an interesting new FLP based on 1,8-diphosphino-naphthanlene phosphine, which combined with $B(C_6F_5)_3$ could easily split H_2.[18] At 60 °C, the resulting phosphonium borate looses H_2 to generate FLP again. Based on this property, such a system has been applied to catalytically reduce silyl-enol ethers at 25 °C under 2 bar of H_2 (Scheme 1.30).

3.2 Catalytic hydrogenations by Amine/Borane FLPs

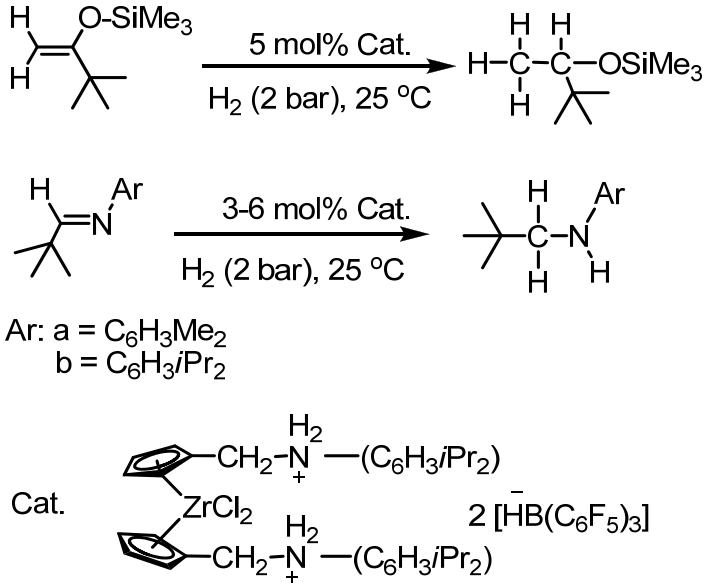


Substrate	Time(h)	Product	Yield (%)
	12		99
	6		99
	12		99
	24		4
	24		4
	6		99
	6		99
	12		85

Scheme 1.31

In a similar fashion, the Repo and Rieger research groups have reported that linked amine-borane species derived from tetramethylpiperidine was capable of activating H_2 heterolytically. Such system was employed in the catalytic hydrogenation of imines and enamines.[35] Generally, this catalyst was effective, affording near quantitative reduction of the substrates, but less bulky imines, like $CH_3N{=}C(H)Ph$ or $CH_3N{=}CCH_2Ph(CH_3)$, were hydrogenated in only 4 % yield (Scheme 1.31).

Bis(arylimino-C_5H_4)$ZrCl_2$ reported by Erker group together with $B(C_6F_5)_3$ could react with H_2 facilely affording the corresponding product zirconocene-bis(ammonium)/2[$HB(C_6F_5)_3$]. The product was proven an efficient hydrogenation catalyst to transfer H^-/H^+ to bulky imines, as well as silyl enol ether under ambient temperatures (Scheme 1.32).



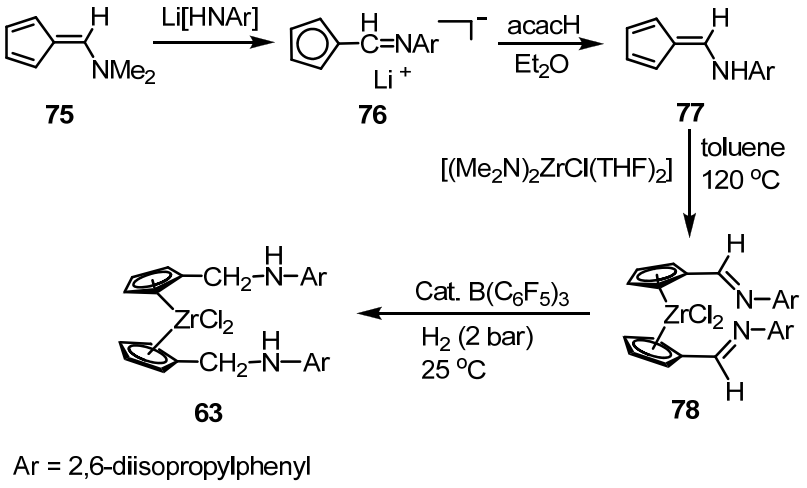
Scheme 1.32

4. Applications of FLPs in Organometallic Chemistry

Generally, it is difficult to transform the typical organic functional-group on many organometallic frameworks, because of the high sensitivity of these metal-containing compounds. This is especially true for air and moisture sensitive early d-block metals and

f-elements.[67-69] Recently, a variety of suitable methods for organic functional-group transformation are beginning to appear to overcome these problems. The latest development of Frustrated Lewis Pairs which were shown to serve as catalyst for the hydrogenation of a series of specific substrates could provide an alternative mild method in synthetic organometallic chemistry.

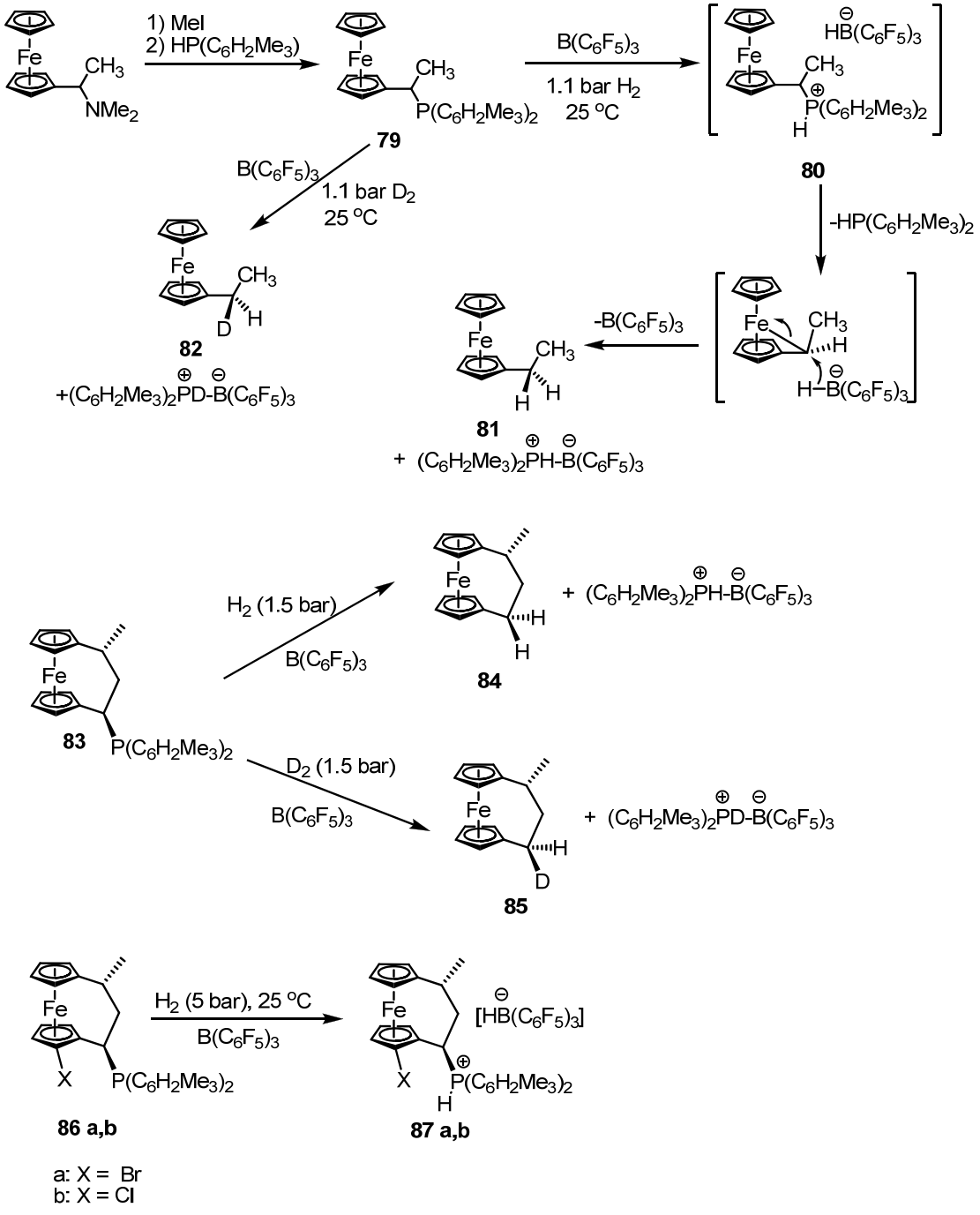
Treatment of 6-dimethylaminofulvene **75** with lithium anilides resulted in the formation of the "imino-Cp" compound **76**, which was then protonated carefully by Brønsted acid acetylacetone giving the N-aryl-substituted 6-aminofulvene **77** (Scheme 1.33). This compound was then reacted with $[(Me_2N)_2ZrCl_2(THF)_2]$ to give product **78**, which forms a Frustrated Lewis Pair with $B(C_6F_5)_3$. But in the presence of a catalytic amount of $B(C_6F_5)_3$, compound **78** could undergo the hydrogenation reaction of the iminio group under H_2 to give the aminomethyl-substituted zirconocene complex **63**, which property has been discussed in **1.2.3**.



Scheme 1.33

Compound (1-(dimesitylphosphino)ethyl)ferrocene **79** was obtained from the reaction of "Ugi's amine" (N,N,-dimethyl-1-ferrocenylethylamine) with methyl iodine and subsequent treated with dimesitylphosphine $((C_6H_2Me_3)_2PH)$.[70] Treatment of compound **79** with $B(C_6F_5)_3$ under H_2 resulted in loss of the phosphine fragment to give ethylferrocene **81**, as well as

$(C_6H_2Me_3)_2PH$-$B(C_6F_5)_3$. It is assumed that compound **79** forms Frustrated Lewis Pairs with $B(C_6F_5)_3$, which cleave H_2 heterolytically under ambient conditions affording the phosphonium cation/hydridoborate anion **80** (Scheme 1.34). It appears that this intermediate is unstable, $(C_6H_2Me_3)_2PH$ was cleaved from the phosphonium cation assisted by the iron



Scheme 1.34

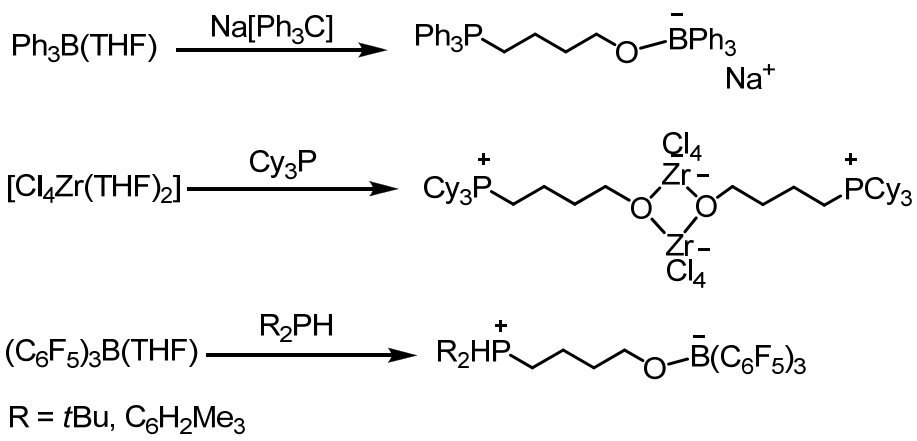
neighboring group followed by nucleophilic hydride attachment from the $[HB(C_6F_5)_3]^-$ anion. The analogous reaction was also observed in the related ferrocenophane series (Scheme 1.34). The observed stereoselective formation of the *trans*-product supported the assumed reaction course when employing D_2 to react with the FLPs of **79**/$B(C_6F_5)_3$ or **83**/$B(C_6F_5)_3$.

Surprisingly, the *ortho*-bromo or *ortho*-iodo substituted ferrocenophane species underwent different reactions with $B(C_6F_5)_3$ under hydrogen condition. The H_2 split product organometallic phosphonium/hydridoborates were stable in these cases, which did not proceed further to release $HP(C_6H_2Me_3)_2$ moiety (Scheme 1.34). This presumably, because of the close contact of PH···halide, which stabilize the $HP(C_6H_2Me_3)_2$ group in the product.

5. Activation of Other Small Molecules by FLPs

5.1 Ring opening of THF by FLPs

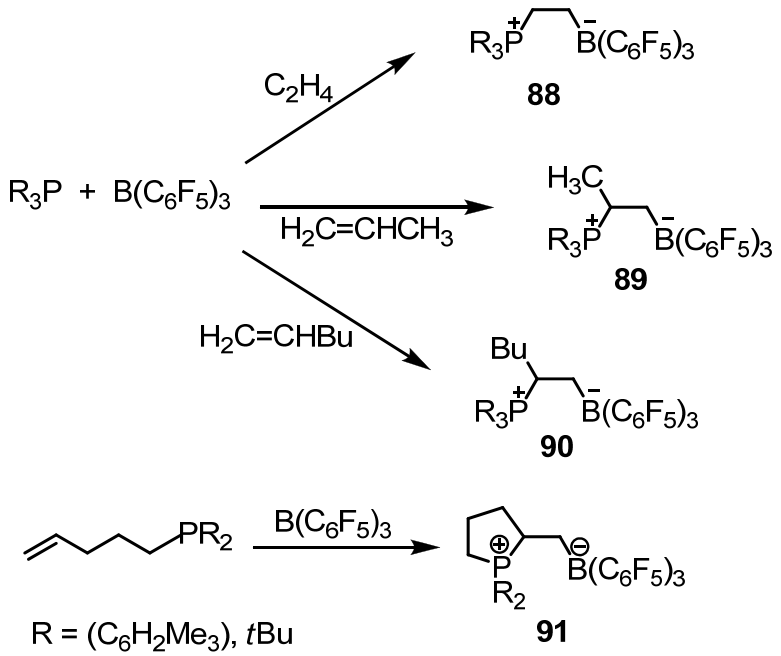
In 1950, Wittig described the reaction of Ph_3CNa with $THF{\cdot}BPh_3$. It is generally observed that the stronger Lewis base simply replace THF to form the stronger Lewis acid/base adduct.[2] However, the reaction proceeded in an unconventional way, the THF was not replaced by the trityl anion, but rather the trityl anion effected the THF ring opening affording the anion $[Ph_3C(CH_2)_4OBPh_3]^-$. Since this early study, a number of systems have been reported to prompt THF ring opening. For example, Lewis acidic transition metals, such as U, Sm, Ti, Zr and main-group Lewis acids including carborane, alane, tellurium species, and boranes in combination with either nitrogen- or phosphorus-based Lewis bases all have been reported to prompt the THF ring opening.[71-79] This unexpected reactivity is mainly due to steric effects of the Lewis acid and Lewis base centers. The most pertinent fact of these to the present discussion is the zwitterionic species $R_2PH(CH_2)_4OB(C_6F_5)_3$ (R = *t*Bu, $C_6H_2Me_3$) derived from the treatment of $(THF)B(C_6F_5)_3$ with sterically encumbered phosphines (Scheme 1.35).[80]



Scheme 1.35

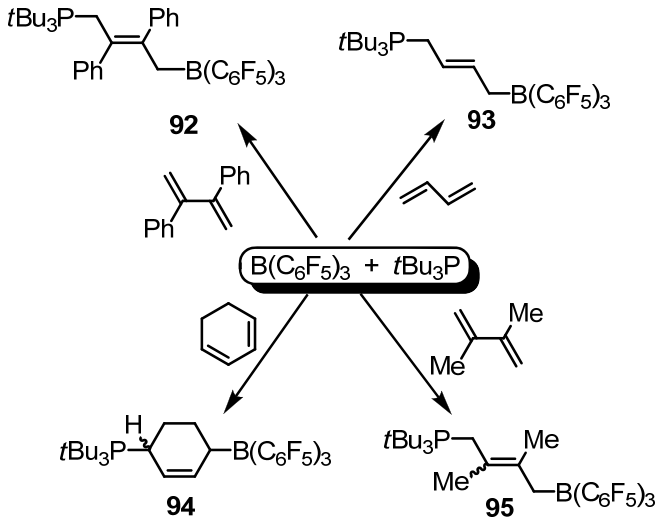
5.2 Activation of Alkenes, Dienes, and Alkynes

The Stephan group has also demonstrated that frustrated Lewis pairs add to alkenes. Addition of ethylene to the combination of $B(C_6F_5)_3$ and R_3P (R = *t*Bu, $C_6H_2Me_3$) resulted in the formation of the zwitterionic species [$tBu_3P(C_2H_4)B(C_6F_5)_3$] (Scheme 1.36).[81] In the same manner, the analogous products derived from the reactions of propylene and 1-hexene with $B(C_6F_5)_3$ and R_3P(R = *t*Bu, $C_6H_2Me_3$), afforded the salts, [$tBu_3PCH(R)CH_2B(C_6F_5)_3$] (R = CH_3, C_4H_9), respectively. In addition, this reaction can also be effected in an intramolecular manner and thus the reaction of CH_2=$CH(CH_2)_3PR_2$ (R = *t*Bu, $C_6H_2Me_3$) with $B(C_6F_5)_3$ generates the cyclic phosphonium borate [$R_2PCH(C_2H_4)CH_2B(C_6F_5)_3$] (R = *t*Bu, $C_6H_2Me_3$). It is noteworthy to point out that in each of these products the boron center adds to the less-hindered carbon center, while the phosphine center connects to the higher substituted carbon. These reactions are also thought to be initiated by the interaction of the Lewis acid with the olefin, prompting attack by the phosphine. IR studies demonstrated the formation of BF_3-ethylene and BF_3-propylene complexes in an argon matrix at 93-125 K would support this assumption.[82] The computational studies also suggested weak π-donation complexes for ethylene-alane and borane adducts.



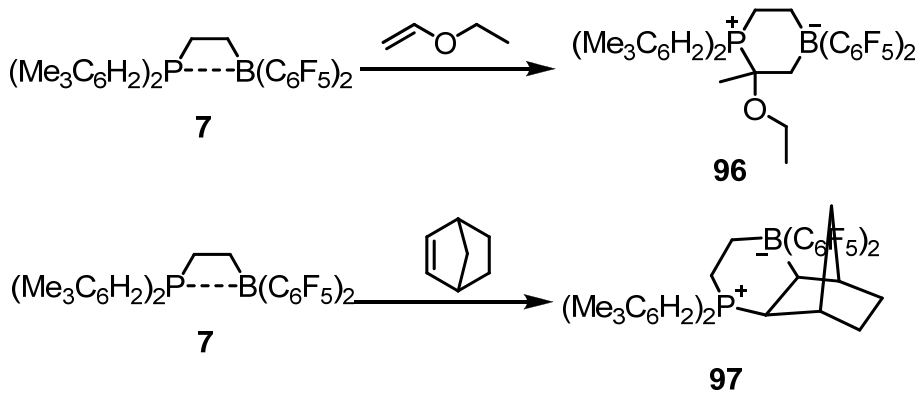
Scheme 1.36

In a closely related series of reactions, combination of FLPs with dienes also results in addition reactions.[83] Combination of an FLPs with the butadiene, 2,3-diphenylbutadiene, 1,3-cyclohexadiene and 2,3-dimethylbutadiene resulted in 1,4-addition as the major products and were isolated in typically 50-60 % yield (Scheme 1.37). These reaction mixture also contain other species that may arise from other stereoisomers or 1,2 addition products.



Scheme 1.37

Erker and co-workers reported that intramolecular Frustrated Lewis Pair **7** to react with the electron-rich olefinic substrate ethyl vinyl ether giving a high regioselective product **96**.[84] When **7** was reacted with norbornene, it selectively undergoes an exo-2,3-addition to norbornene affording product **97** (Scheme 1.38). Based on experimental and theoretical evidence, this reaction presumably takes place in an asynchronous concerted fashion with the B-C bonding formed in slight preference to the P-C bond.

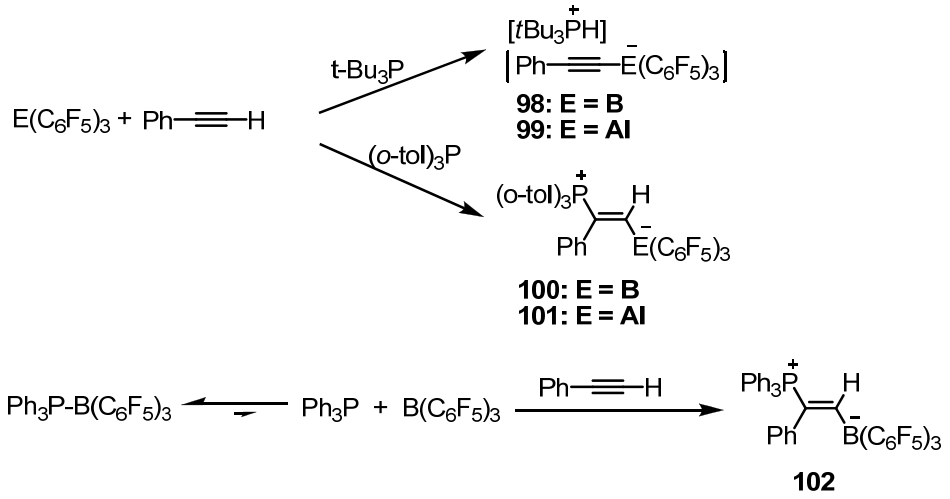


Scheme 1.38

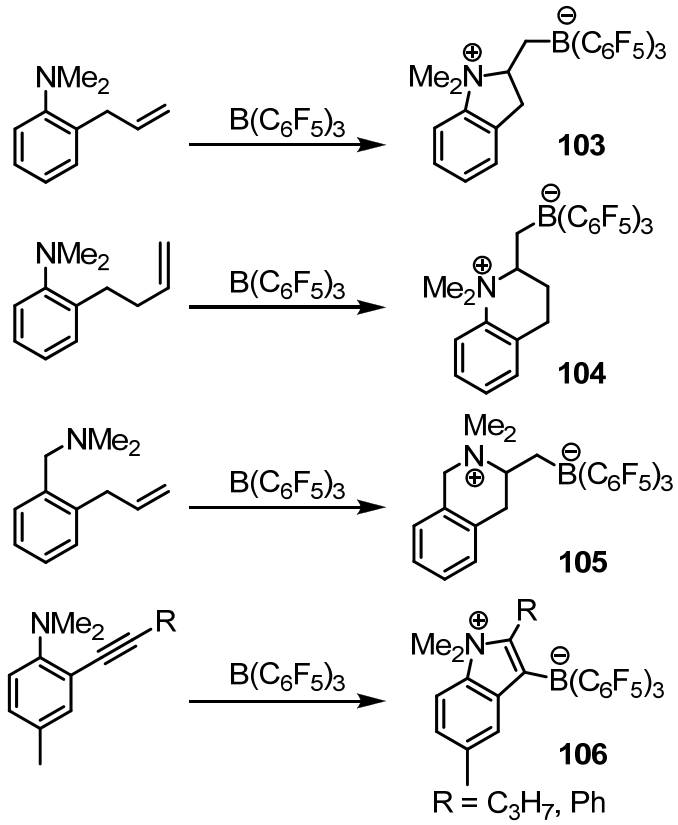
Furthermore, the FLPs also can add to alkynes, which usually proceed along two different pathways. The FLP either promotes 1,2-addition reaction with substituted terminal alkynes to yield donor/acceptor substituted alkenes of type **100** and **101** or undergoes C-H deprotonation to establish ionic products of type 9**8** and **99** (Scheme 1.39).[85] The classical Lewis adduct Ph_3P-$B(C_6F_5)_3$ also underwent an 1,2-addition reaction with PhC≡CH to give product **102**. This result infers an equilibrium involving some degree of dissociation of PPh_3 from the classical adduct Ph_3P-$B(C_6F_5)_3$, but no evidence of dissociation is found by NMR spectroscopy. These observations suggest the possibility that a broad new range of Frustrated Lewis Pair reactivity is accessible from classical Lewis adducts, which previously were thought to be unreactive.

Quite recently, Stephan and Erker demonstrated that FLP reactivity can be exploited to effect intramolecular cyclizations of sterically encumbered amine with olefin and acetylene fragments. They synthesized a series of five- and six-membered heterocyclic derivatives

(Scheme 1.40).[86]



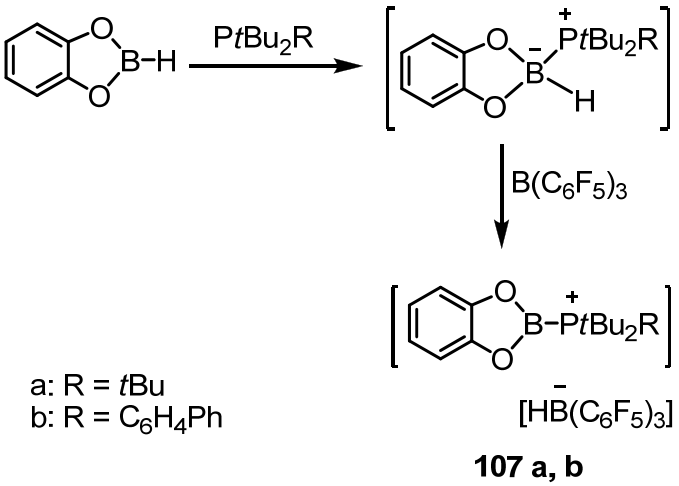
Scheme 1.39



Scheme 1.40

5.3 Activation of B-H bonds by FLPs

The unquenched Lewis acidity and basicity of Frustrated Lewis Pairs can cooperate to effect the activation of B-H bonds in catechol borane, resulting in the formation of $[t\text{Bu}_2\text{RPBO}_2(\text{C}_6\text{H}_4)][\text{HB}(\text{C}_6\text{F}_5)_3]$ **107** (Scheme 1.41).[87] It assumed that the phosphine initially coordinates to catechol borane, which enhances the hydridic character of the B-H bond. Subsequently $\text{B}(\text{C}_6\text{F}_5)_3$ abstracted the hydride from the adduct to give the product **107**. The unusual cation $[t\text{Bu}_2\text{RPBO}_2(\text{C}_6\text{H}_4)]^+$ could be viewed as a phosphine stabilized borenium cation or alternatively as a borylphosphinium cation. The computations support the location of the positive charge on P and thus the latter formulation.

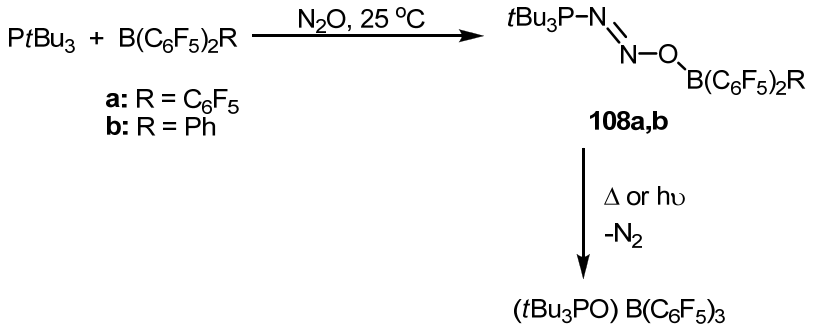


Scheme 1.41

5.4 Activation of N_2O and CO_2 by FLPs

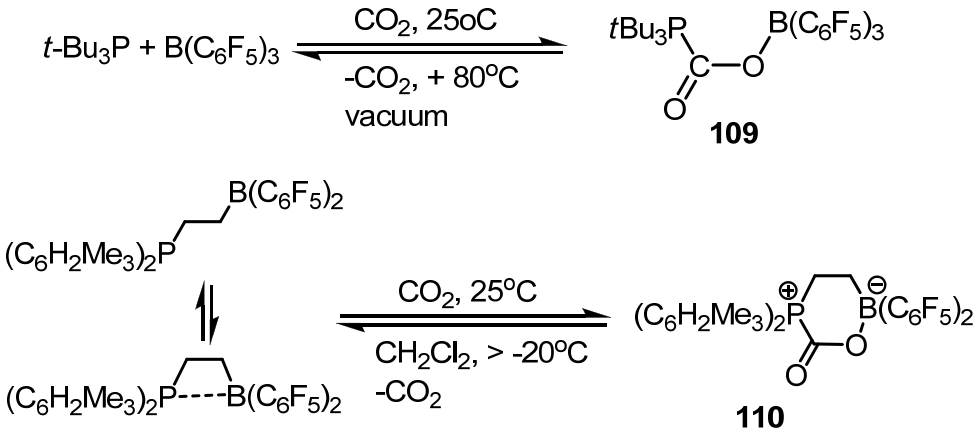
The reaction of an equivemolar mixture of *t*-Bu_3P and $\text{B}(\text{C}_6\text{F}_5)_3$ with N_2O (1 bar) resulted in the formation of the zwitterionic product $t\text{Bu}_3\text{P-N=N-O-B}(\text{C}_6\text{F}_5)_3$ **108a** (Scheme 1.42).[88] When employing less basic phosphines, like $(o\text{-tolyl})_3\text{P}$, together with $\text{B}(\text{C}_6\text{F}_5)_3$, no evidence was formed that such FLP reacted with N_2O. While, Lewis acid was no longer restricted to the very Lewis acidic borane $\text{B}(\text{C}_6\text{F}_5)_3$. Treatment of $t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_2\text{Ph}$, a substantially weaker Lewis acid than $\text{B}(\text{C}_6\text{F}_5)_3$, with N_2O (1 bar) gave the product **108b**. Heating the NMR sample of **108a** in $\text{C}_6\text{D}_5\text{Br}$ at 135 ^{o}C for 44 h or photolysis of **108a** resulted in the liberation of

N_2 and formation of the Lewis acid-base adduct (tBu$_3$P=O)B(C_6F_5)$_3$. This result was supported by computation which showed that extrusion of N_2 and formation of tBu$_3$P=O and B(C_6F_5)$_3$ from **108a** is thermodynamically favorable by 60.4 kcal/mol relative to **108a**.



Scheme 1.42

In a collaborative report, Stephan et al. and Erker et al. found that CO_2 reacts with Frustrated Lewis Pairs in a straightforward fashion. Combination of the FLP tBu$_3$P···B(C_6F_5)$_3$ with CO_2 at ambient condition which yielded the product tBu$_3$P-C(O)O-B(C_6F_5)$_3$ **109** (Scheme 1.43).[89] Similar reaction also occurred between the intramolecular Frustrated Lewis Pair ($C_6H_2Me_3$)$_2$PCH_2CH_2B(C_6F_5)$_2$ and CO_2, affording product **110**. The thermal stabilities of these two products **109** and **110** were examined. Heating a solution of **109** in bromobenzene to 80 °C for 5 h resulted in the liberation of about 50% of the CO_2. In contrast, **110** is stable as a solid, it rapidly looses CO_2 in dichloromethane or toluene above approximately -20 °C to

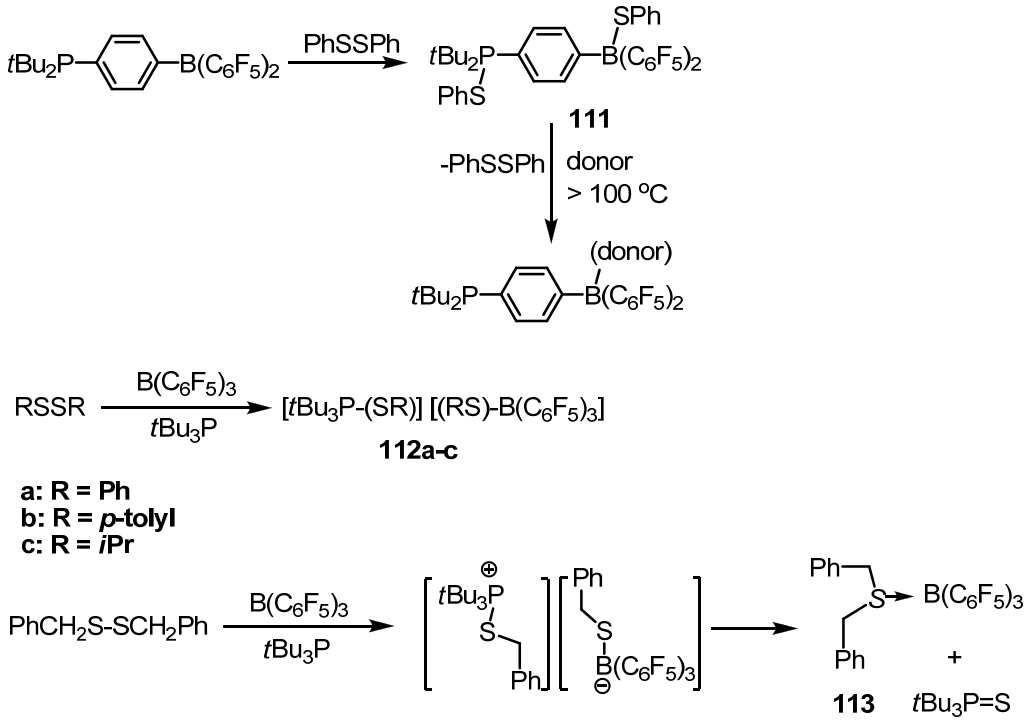


Scheme 1.43

cleanly re-form the starting material. This indicated that the CO_2 addition reaction by FLPs can be reversible.

5.5 Activation of S-S bonds by FLPs

The Stephan group has reported that the FLPs could also effect S-S bonds of disulfide to heterolytically be cleaved, affording formally sulfenium cations stabilized by phosphine group and the corresponding thio-borate anion. The addition of diphenyl disulfide PhSSPh to intramolecule FLP tBu$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ affords the zwitterionic phosphonium borate [tBu$_2$P(SPh)(C$_6$F$_4$)B(SPh)(C$_6$F$_5$)$_2$] **111**. While in the presence of a base such as PMe$_3$ or a donor solvent such as THF at elevated temperature (> 100 ^{o}C), product **111** would liberate disulfide and form the base coordinated phosphino-borane [tBu$_2$P(C$_6$F$_4$)B(donor)(C$_6$F$_5$)$_2$] (Scheme 1.44).[90]



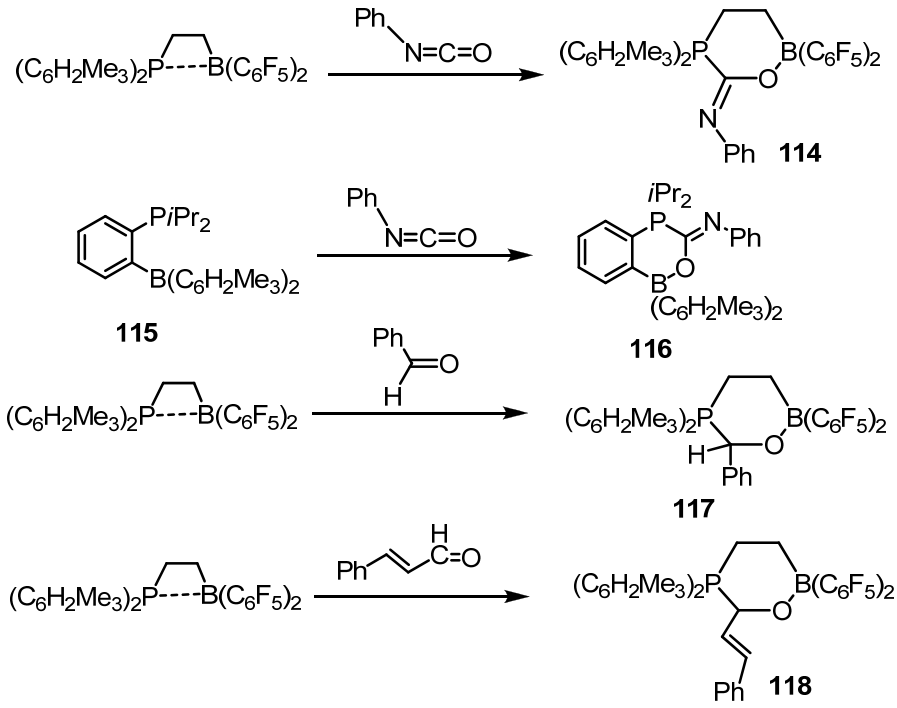
Scheme 1.44

In a similar fashion, the intermolecular FLP t-Bu$_3$P/B(C$_6$F$_5$)$_3$ reacted with RSSR to give

[*t*-$Bu_3P(SR)$][$(RS)B(C_6F_5)_3$] (R = Ph, *p*-tolyl, *i*Pr) (**112a-c**). In contrast, the corresponding reaction of BnSSBn with FLP *t*$Bu_3P/B(C_6F_5)_3$ yields a 1:1:1 mixture of *t*Bu_3P=S, Bn_2S, and $B(C_6F_5)_3$. This reaction is thought to proceed via the transient formation of the salt [*t*$Bu_3P(SBn)$][$(SBn)B(C_6F_5)_3$], with a subsequent benzyl group transfer from the cation to the S of the anion, yielding *t*Bu_3P=S, $Bn_2S{\cdot}B(C_6F_5)_3$ (Scheme 1.44). The contrasting reactivities presumably exist, because of a diminished steric demand permitting facile approach of the transient cation to effect alkyl group transfer.

5.6 Activation of Carbonyl groups by FLPs

Frustrated Lewis Pairs undergo 1,2-addition reactions to carbonyl compounds. Treatment of the intramolecular FLP $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$ and $(iPr)_2P(C_6H_4)B(C_6H_2Me_3)_2$ with phenylisocyanate resulted in the formation of the six-membered heterocycle compounds **114** and **116** (Scheme 1.45). A similar reaction also happened between



Scheme 1.45

$(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$ and benzaldehyde. In the case of cinnamic aldehyde, the reaction has a selectivity choice: the P/B 1,2-addition could take place either on the C=C or the C=O functional group, or it undergoes 1,4-additon. The results showed that 1,2-addition to the carbonyl group is the unique reaction product.[84]

6. Motivation of the Thesis

The advent of FLP reactivity brought up new perspectives to the realm of small molecule activation and application in catalysis.

Following Stephan group's pioneering work, a great number of FLPs were reported to activate H_2 or other small molecules. The Lewis base is no longer limited to phosphine centers, but also extended to sterically demanding amines, imines, or N-hereocycylic carbenes. While the influence of the Lewis acid has up to now been studied less, the main Lewis acid to be used as $B(C_6F_5)_3$. This thesis work is mainly focusing on modulating the Lewis acid part. Employ modified Lewis acids in FLP chemistry to activate small molecules. In addition, try to get detailed experimental information to explain the H_2 activation process by FLPs through variations in the Lewis acids. Though various mechanisms have been proposed based on computational results, there is still lack of experimental support. Besides, exploration of new reactivity by FLPs is sought. Despite the fact that FLPs were only first described 3 years ago, it is evident that a great variety of opportunities for new reactivity and catalysis can be expected.

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Metal-free hydrogen activation and hydrogenation of imines by 1,8-Bis(dipentafluorophenylboryl)naphthalene

Abstract

In the presence of 2,2,6,6-tetramethylpiperidine (**TMP**) or tri-*tert*-butylphosphine (*t*-Bu_3P), 1,8-bis(dipentafluorophenylboryl)naphthalene has been found to activate H_2 heterolytically and to hydrogenate various imines under mild conditions.

Introduction

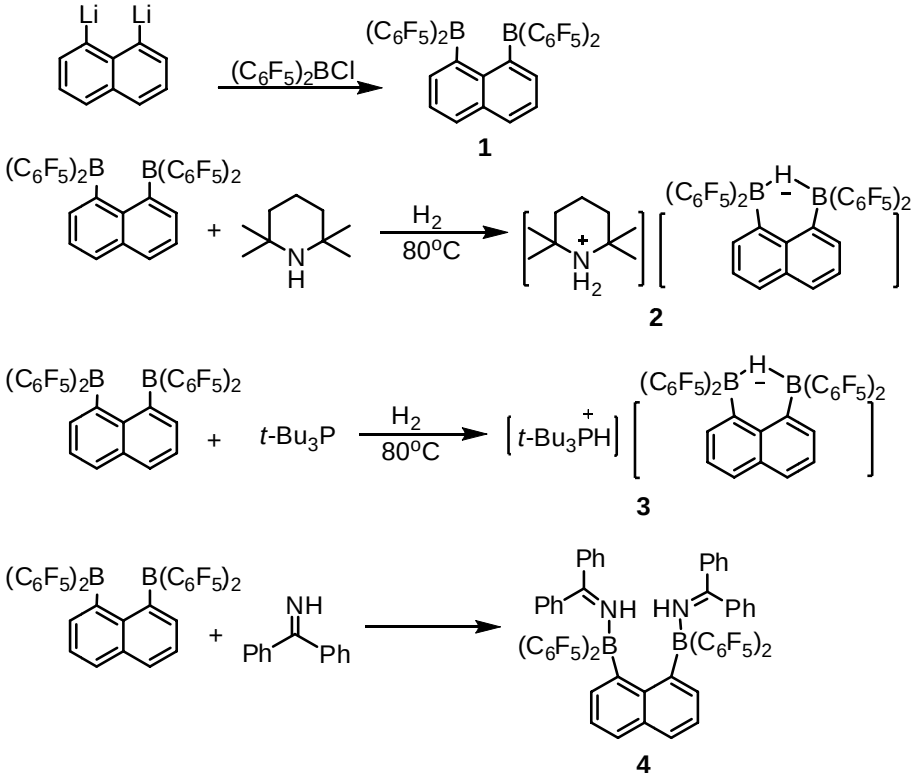
In 2006 Stephan et al. discovered that "metal-free" main group element Lewis acid/base pairs, like $Mes_2P(C_6F_4)B(C_6F_5)_2$[1], can reversibly activate H_2. This finding triggered a search for a new type of hydrogenation catalysts. Similar to protonic-hydridic transition metal complexes such hydrogenation systems operate via a "bifunctional activation" or "ionic hydrogenation" mode with formal heterolysis of H_2. For proper reactivity such Lewis pairs are expected not to be fully paired rather to establish only loose contact in the form of encounter complexes of "Frustrated Lewis Pairs" (FLPs).[2,3] As one of the fruitful results of this concept similar "FLP" systems were found to enable activating of H_2 or other small molecules.[4-15] This remarkable finding could then be developed to catalysts for metal-free hydrogenations of imines, nitriles and aziridines, as well as enamines and C=C double bonds of silyl ethers.[16-19] The range of the FLPs could then be extended to boron/carbene systems, in which the steric demand of the carbene substituents were found to be very crucial to the FLP reactivity.[7,8] On a related issue the Rieger group used borane/amines pairs to tune heterolytic H_2 activation further.[9] However, the influence of the Lewis acid was up to now studied less.[5,11-12] We reckoned that a probing of bidentate Lewis acids with both Lewis acidic centers in close vicinity would offer great opportunity to create enhanced reactivity via an increase in

Lewis acidity and/or utilization of neighboring effects.[20] 1,8-Diboryl-naphthalene derivatives involving two strong, proximal Lewis acidic boron centers were found to advance to the stage of "superelectrophiles". For instance 1,8-bis(dimethylboryl) naphthalene was shown to perfectly chelate small anions, such as hydride or fluoride.[21-22] 1,8-bis(diphenylboryl)naphthalene was found to cage an electron between the two boron atoms generating a long one electron "σ-bond". The empty *p* orbitals of the neighboring boron centers are thought to overlap and generate an energetically extraordinarily low-lying LUMO "super" Lewis acidic in character.[23] We therefore approached the preparation of 1,8-bis(dipentafluorophenylboryl)naphthalene **1** (Scheme 2.1) and expected that **1** would react with H_2 in the presence of a bulky Lewis base taking also advantage of unique bidentate geometry.

Results and discussion

Treatment of 1,8-dilithionaphthalene[24-25] with 2 equiv of chlorodi(pentafluoro phenyl)borane[26] in toluene afforded 1,8-bis(dipentafluoro phenylboryl)naphthalene (**1**) as a yellow solid in 25% yield. The ^{19}F NMR spectrum [δ -127.4 (*o*-), -145.9 (*p*-), -161.8 (*m*-C_6F_5) (d_8-toluene)] was consistent with the presence of three-coordinate boron centers ($\Delta\delta_{m,p}$ = 15.9). The ^{1}H NMR spectrum also supported the diboryl substituted naphthalene structure (δ 7.61 (d, 2H), 7.41 (d, 2H), 7.10 (t, 2H)). A single-crystal X-ray analysis revealed a sterically quite congested molecule (Figure 2.1). The tight geometry induces significant distortion of the naphthalenediyl fragments with distorted C(1)-C(10)-B(2) (126.42(2)°) and C(1)-C(2)-B(1) (126.08(4)°) "sp^2" angles. Each boron center nevertheless adopts a distorted trigonal planar arrangement with a B1···B2 non-bonding distance of 3.26(1) Å, however, considerably longer than the B···B distance in 1,8-bis(diphenylboryl) naphthalene (3.00(2)Å).[23] Steric congestion of the phenyl rings causes tilting of the trigonal boron planes with a large dihedral angle between them (42.8 and 42.1°). This forces the vacant boron p_B orbitals out of conjugation with the naphthalene rings enhancing Lewis acidity. This would imply that the boron centers possess Lewis acidity at least in the range of the highly Lewis acidic monofunctional boranes

$RB(C_6F_5)_2$ (R = alkly, alkenyl, aryl, C_6F_5).



Scheme 2.1

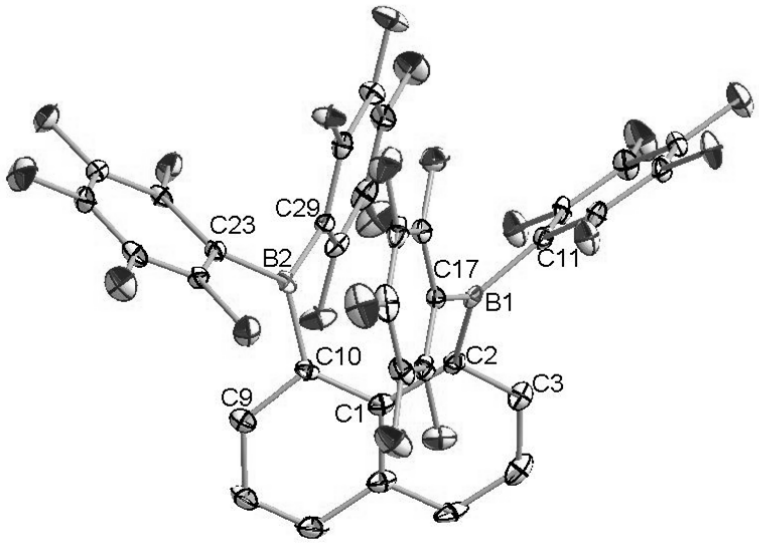


*Figure 2.1 Molecular structure of compound **1**. Hydrogen atoms are omitted for clarity.*

Treatment of complex **1** with 2,2,6,6-tetramethylpiperidine (**TMP**) or *t*-Bu_3P under H_2 atmosphere (1.5 bar) resulted at 80°C in the formation of the white H_2 splitting products **2** and **3** in *ca* 23% and 32% yield (Scheme 2.1). It featured a broad ^1H NMR hydride resonance at 2.89 ppm (B*H*B) and a signal for the acidic H_N of the ammonium component at 2.11 ppm for compound **2**. The P*H* resonance of compound **3** located at 4.69 ppm in ^1H NMR spectrum with $^1J_{HP}$ couplings of 430 Hz, and in the ^{31}P NMR the corresponding resonance was found at 60.7 ppm. ^{19}F NMR spectroscopy furnished signals at δ -129.8 (*o*), -159.6 (*p*), -166.3 (*m*-F) ppm for compound **2** and at δ -130.2 (*o*), -161.2(*p*), -167.0 (*m*-F) ppm for compound **3** with $\Delta\delta$ (*m*-F)-(*p*-F) separation of consistent with tetracoordinate boron. An X-ray crystallographic study of **2** revealed that the unit cell contained two independent molecules (see Figure S1 in supporting information). Figure 2.2 shows only one of these. In both independent molecules the hydride atoms were located in bridging position. For one molecule the B-H-B angle is 121(3)° (B1-H1A-B2) and for the other molecule is 143(3)° (B3-H1B-B4). The B1-H1A and B2-H1A bond lengths are 1.45(5) and 1.41(5) Å, while B3-H1B and B4-H1B are 1.31(5) and 1.36(5) Å. The non-bonding separations between B1···B2 and B3···B4 are 2.491(8) and 2.534(8) Å, respectively,

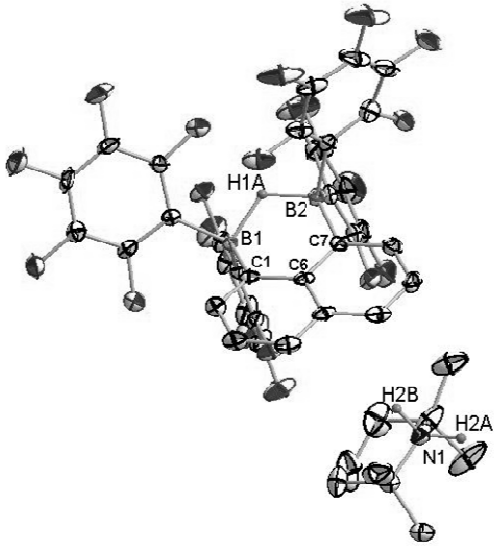


Figure 2.2 Molecular structure of compound 2. Hydrogen atoms except for BH and NH are omitted for clarity.

Selected bond lengths [Å] and Selected bond angles [°] of Compound **1-3**

Compound 1					
B1-C2	1.542(4)	B1-C11	1.585(3)	B1-C17	1.585(4)
B2-C10	1.542(3)	B2-C23	1.580(3)	B2-C29	1.576(3)
C2-B1-C17	120.9(2)	C2-B1-C11	119.7(2)	C17-B1-C11	118.1(2)
C10-B2-C29	120.2(2)	C10-B2-C23	120.9(2)	C29-B2-C23	117.9(2)
C1-C10-B2	126.4(2)	C1-C2-B1	126.1(2)		
Compound 2					
B1-H1A	1.46(4)	B2-H1A	1.41(4)	N1-H2A	0.88(3)
N1-H2B	0.87(4)	C6-C1-B1	118.5(4)	C6-C7-B2	120.3(5)
C1-B1-H1A	108.5(16)	C7-B2-H1A	113.0(15)	C1-C6-C7	120.0(4)
Compound 3					
B1-H1A	1.51(2)	B2-H1A	1.45(2)	P1-H1B	1.39(2)
C1-B1-H1A	113.0(9)	C7-B2-H1A	111.0(9)	C6-C1-B1	121.6(2)
C7-C6-C1	119.9(2)	C6-C7-B2	118.8(2)	B1-H1A-B2	118.24(2)

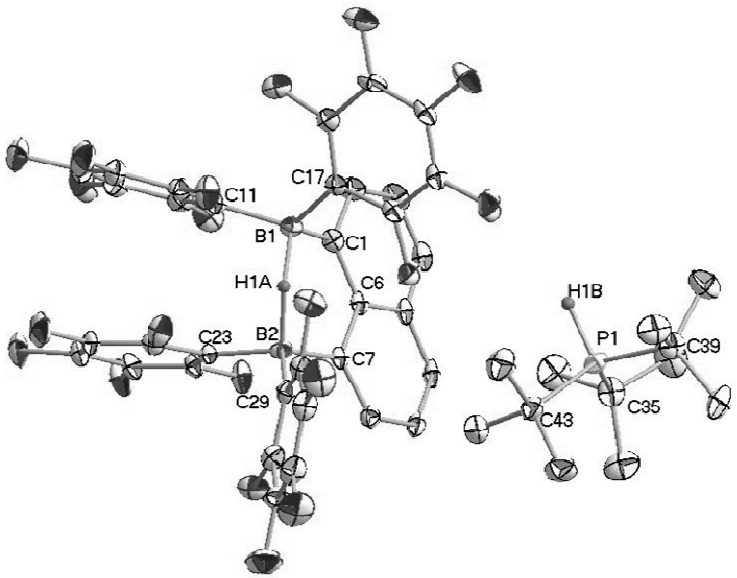


Figure 2.3 Molecular structure of compound 3. Hydrogen atoms except for BH and PH are omitted for clarity

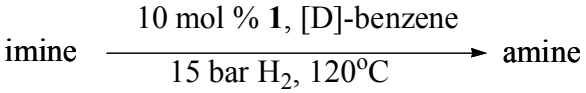
which are compressed with respect to the related one of **1**. Unlike in a recently reported ion paired structure of the splitting H_2 by a FLP, the corresponding B-H and N-H are not oriented towards each other to form a dihydrogen bond.[4,9] Instead, the ions of **2** are found connected through multiple weak C-H···F hydrogen bonding interactions. The X-ray

structural analysis of compound **3** showed that it has the similar anion as those in compound **2**, the hydride is in the bridging position compressed the two boron centers to 2.54 Å. The bridging angle of B1-H1A-B2 in this case is 118.24° (Figure 2.3).

Further investigations demonstrated that **1** is an efficient "ionic hydrogenation" catalyst for imines transferring H^+/H^- as a H_2 equivalent. Table 2.1 summarizes the results for catalytic hydrogenation of imines. Under rigorous exclusion of water and under 15 bar of H_2 in the presence of 10 mol % of **1** conversion to the corresponding amines was achieved in yields of 99 % within 1 h at 120 ^oC except for PhCH=NPh (Table 2.1, entry 3) and the sterically less demanding phenyl benzyl imine (Table 2.1, entry 4). The TOFs of the catalytic reaction of the phenyl diphenyl imine (Table 2.1, entry 1) were found to be linearly dependent on the H_2 pressure and thus demonstrated first order dependence in H_2. This allowed concluding that the H_2 splitting reaction significantly contributes to the rate determining steps or is the rate determining step of the catalytic cycle (see Figure S1). When benzophenone imine was used as a substrate, the Lewis adduct **4** was formed (Scheme 2.1). The crystal structure of this adduct (Figure S4) revealed a strongly distorted and strained geometry of the naphthalenediyl fragment. The benzophenone imines are each connected to one tetrahedral boron center causing a long non-bonding B···B distance of 3.851(5) and 3.870(5) Å. The imines seemingly attacked **1** at the distal sides of the boron planes. The averaged B-N bond distance of 1.60 Å correspond to a "normal" B-N bond. Thermal B-N dissociation required for H_2 splitting seems therefore quite unlikely.

By analogy to earlier suggestions for a catalytic hydrogenation of imines with $B(C_6F_5)_3$,[27-28] the mechanism would involve first heterolytic H_2 splitting by the imine/borane FLP to generate an iminium hydridoborate ion pair appearing in low concentration (Scheme 2.2). This step is then followed by hydride transfer from the $[BH]^-$ unit to the iminium carbon and subsequent dissociation of the boron–amine adduct liberating the catalyst, as well as the amine product. None of the imines of the entries E1-E7 of Table 2.1 was able to heterolytically split H_2 in the presence of **1** at room temperature in a spectroscopically relevant amount. Heterolytic H_2 splitting with any of the FLPs takes place only at elevated temperatures generating the iminium hydridoborate ion pair. In this context it is interesting to

Table 2.1 Catalytic hydrogenation of imines by compound **1** and H_2.

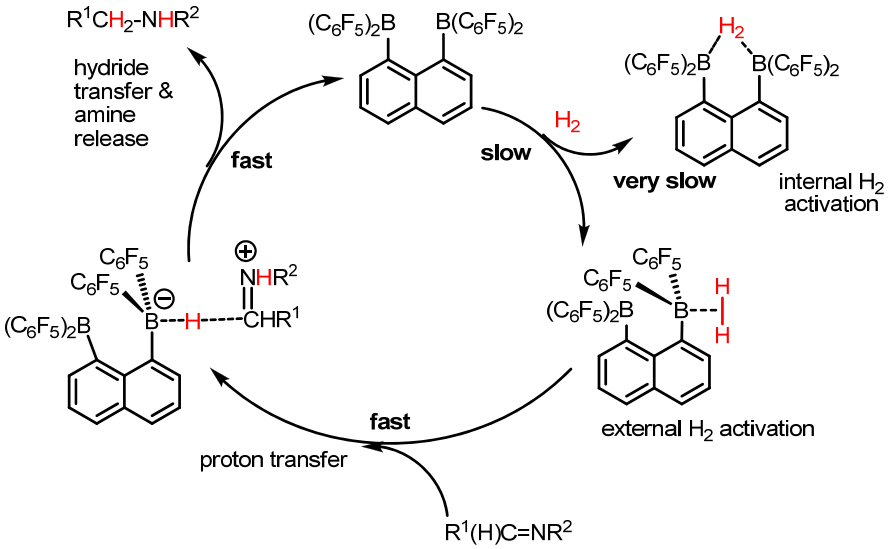


Entry	Imine	t (h)	Amine	Yield (%)	TOF
1	$PhCH{=}NCHPh_2$ [a]	1	$PhCH_2NHCHPh_2$	> 99	20/h
2	PhCH=N*t*Bu	1	$PhCH_2NH$*t*Bu	> 99	10/h
3	PhCH=NPh	1	$PhCH_2NHPh$	78	8/h
4	$PhCH{=}NCH_2Ph$	6	$PhCH_2NHCH_2Ph$	< 5 %	
5	$PhCH{=}NC_6H_4Cl$-*p*	1	$PhCH_2NHC_6H_4Cl$-*p*	> 99	10/h
6	*p*-$ClC_6H_4CH{=}NC_6H_4Cl$-*p*	1	*p*-$ClC_6H_4CH_2NHC_6H_4Cl$-*p*	> 99	10/h
7	*p*-$NO_2C_6H_4CH{=}NPh$	1	*p*-$NO_2C_6H_4CH_2NHPh$	> 99	10/h

a) 5 mol % of compound **1**.

note that when **2** and the iminium salt [PhCH=NH*t*Bu][BF_4] were mixed in a 1 : 1 ratio, hydride transfer to the iminium part and concomitant amine formation could not be observed even at 120 °C. We concluded from this experiment that in the catalytic reaction the anion of **1** with "internal" H^- binding is presumably not an intermediate, rather an "external" species with the hydride connected to only one boron center and facing to the outside (Scheme 2.2). Consequently the intermolecular hydride transfer to the iminium with formation of the amine occurs aslo externally. Probing another internal mechanistic possibility, we attempted the reaction of **2** with PhCH=N*t*Bu, which however did not insert into the B-H-B bond to generate an amide complex, which demonstrated again that it is less plausible to assume that the anion of hydride **2** is an intermediate of the catalytic cycle of Scheme 2.2.

The final step of the catalytic cycle the dissociation of the B-N adduct to free the catalyst and the amines is often considered to be rate-determining,[27] however, this seems different for the catalyses with **1**. The quite congested geometries of the amine adducts with **1** would not allow proper B-N interactions tight enough to render under catalytic circumstances rate determining dissociation. Therefore, in case the catalytic imine hydrogenation with **1** is suppressed, this seems not to originate from a too tight amine-boron adduct rather from the too low kinetic H_2 affinity of **1**. "Internal" access of H_2 penetrating into the gap between



Scheme 2.2

both boron centers, the "super Lewis acidic activation pathway", apparently possesses a higher barrier than the "external" access of H_2 approaching just one boron center from the outside. Therefore in catalytic reactions **1** behaves obviously one-centered and related to the corresponding imine/$B(C_6F_5)_3$ FLP's. This was further substantiated by a comparison of the hydrogenation activities of **1** and $B(C_6F_5)_3$ with various imines displaying somewhat better performance for $B(C_6F_5)_3$; but overall both types of reactions were kinetically in the same range (Table S1). We then tested the H_2 pressure dependence of the reaction of $PhCH{=}NCHPh_2$ with $B(C_6F_5)_3$ and found that under identical conditions as for **1**, the TOF curve initially increased linearly with pressure and reached a TOF of 20 h^{-1} at 5 bar of H_2 (Figure. S2).

Attempts to trace interaction of H_2 with the double Lewis acid **1** via ^1H and ^{19}F NMR spectroscopy at temperature as low as 193 K were not successful, which might suggest that the formation a more stable and observable internal **1**-H_2 adduct has a high barrier to form, while the external **1**-H_2 adduct is relatively unstable - similar to the $B(C_6F_5)_3$ cases - and too short-lived to be identified with conventional analytical methodologies. Nevertheless H_2 adduct formation and splitting must occur in transient catalytic intermediates, otherwise hydrogenation catalysis could not be envisaged.

In summary, we could prepare the novel bidentate Lewis acid 1,8-bis(dipentafluorophenylboryl)naphthalene, which showed heterolytic splitting of H_2 with **TMP** and *t*-Bu_3P. It also proved to be a good catalyst for the direct hydrogenation of imines. Further detailed mechanistic investigations of the FLP with double Lewis acids are sought to allow eventually full insight into the reaction course enabling "fine tuning" in the search for even more functional bidentate Lewis acids.

Experimental part

General consideration: All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze-thaw cycles prior to use. All organic reagents were purchased from Aldrich and used without further purification. 25 mL steel autoclave was used for the catalytic reaction.

^1H NMR, ^{19}F NMR and $^{11}B\{^1H\}$ NMR data were recorded on a Varian Gemini-200 spectrometer. Chemical shift are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F NMR, $^{11}B\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR were referenced to $CFCl_3$, $BF_3{\cdot}OEt_2$, 85% H_3PO_4, respectively. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Microanalyses were carried out at the Anorganisch-Chemisches Institute of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoKα radiation, λ = 0.71073 Å).[29] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction[30] and data reduction were performed with the Oxford program suite *CrysAlisPro*.[31] The structures were solved with direct methods (*SHELXS-97*) and were refined by full-matrix least-squares methods on F^2 (*SHELXL-97*).[32] All programs used during the

crystal structure determination processes are included in the *WINGX* software.[33] The program *PLATON*[34] was used to check the result of the X-ray analyses.

The crystal structure of **1** contains one molecule per asymmetric unit. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H distances of 0.95 Å and their isotropic displacement parameters constrained to 1.2 times the value of U_{eq} of the carbon atom it binds to. No classic hydrogen bonds found.

The asymmetric unit of **2** consists of six crystallographically independent species: two 2,2,4,4-tetramethylpiperidinium, two 1,8-bis(dipentafluorophenylhydroboryl)-naphthalene and two solvent molecules of benzene. The hydrogen atoms on B1, B3, N1 and N2 were located and either freely refined (on B1 and B3) or softly restrained (on N1 and N2). One solvent molecule of benzene is positionally disordered in a ratio 0.47:0.53. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C—H distances of 0.93 - 0.97 Å and their isotropic displacement parameters constrained to 1.2 or 1.5 times the value of U_{eq} of the atom it binds to. No classical hydrogen bonds found. Despite a selected crystal with a suitable size (0.24 × 0.14 × 0.12 mm^3) the ratio observed / unique reflections was quite low and may be responsible of the relatively high R_{int} observed.

The crystal structure of **4** consists of two crystallographically independent molecules of bis(dipentafluorophenylboryl)-naphthalene-dibenzophenoneimine and solvent molecules of chloroform and hexane. Restraints were used to correct the geometry of the hexane molecule (with *DFIX* and *DANG*) and the thermal parameters of the hexane molecule and one of the two chloroform molecules (with *EADP*). Both molecules of chloroform are positionally disordered (0.50:0.50 and 0.34:0.66). All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H distances of 0.93 Å and N—H distances of 0.86 Å and their isotropic displacement parameters constrained to 1.2 times the value of U_{eq} of the atom it binds to. No classic hydrogen bonds found.

There is one relatively "strong" residual peak (Q1 = 2.45 $e^-.Å^{-3}$) located at 1.2 Å from C126 of the solvent molecule of hexane. The solvent molecule of hexane lies on a special position (center of inversion) which led to refine only one half of the molecule. One can not exclude the fact that the molecule is disordered or partially disordered about the crystallographic inversion

center or that the molecule does not fully occupy the site but among the possible refinements the chosen one was the most satisfactory. F23 exhibits a cigar-shaped ellipsoid like its near carbon or fluorine neighbours. It seems that the whole corresponding C_6F_5 ligand could be very slightly disordered over two positions, but it is not sufficiently significant to be refined in a different way. The splitting of the sole F23 would be meaningless.

Preparation of compound 1[35]

In a 100mL flask, under N_2, (0.52g, 1.36 mmol) diiodonaphthalene[36] was dissolved in 30 mL dry toluene. The solution was cooled to -78°C with stirring, 1.7mL (2.7mmol) of a solution of n-butyl lithium (1.6M in hexane) was added dropwise with a syringe. The solution became dark brown, and allowed to stir for 2h at -78°C. Then a solution of chlorodi(pentafluorophenyl)borane[37] (1.03g, 2.7mmol) in 10mL toluene was added slowly through a cannula. The solution became orange in color, and was allowed to warm temperature. After 20h of stirring at room temperature, removed some precipitation through filtration and the solvent was removed *in vacuo* to half volume and hexane was added to promote precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as yellow solid. Yield: 25 %. Crystals were obtained from toluene solution at -35 °C. Anal. Calcd for $C_{34}H_6B_2F_{20}$: C, 50.04; H, 0.74. Found: C, 49.97; H, 0.80. ^{1}H NMR (toluene-d_8, 200 MHz, 293 K): δ = 7.61 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.41 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.10 ppm (t, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*). ^{19}F NMR (toluene-d_8, 188 MHz, 293 K): δ = -127.4 (d, 8F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -145.9 (t, 4F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -161.8 ppm (t, 8F, $^3J_{FF}$ = 19 Hz, *m*-C_6F_5). ^{13}C {^{1}H} NMR (toluene-d_8, 50 MHz, 293 K): δ = 112.9 (B-*C*), 133.7 (C-3,6), 136.9 (C-4,5), 137.9 (dm, $^1J_{C-F}$ = 250 Hz, *m*-C_6F_5), 139.4 (C-10), 141.3 (C-2,7), 144.7 (C-9), 144.9 (dm, $^1J_{C-F}$ = 252 Hz, *p*-C_6F_5), 147.2 (C-1,8), 149.0 ppm (dm, $^1J_{C-F}$ = 252 Hz, *o*- C_6F_5).

X-ray Crystal Structure Analysis of **1**: formula $C_{34}H_6B_2F_{20}$, *M*r = 816.01, Triclinic, $P\bar{1}$, a = 10.5171(4), b = 11.9691(4), c = 14.0547(5) Å, α = 69.240(3), β = 84.669(3), γ = 66.772(4)°, V = 1517.98(11) Å^3, Z = 2, μ = 0.189 mm^{-1}, 17221 reflections collected, 6206 independent (R_{int} = 0.0386), R_1 = 0.0448, wR_2 = 0.0770 (for 3517 observed reflections with $I \geq 2\sigma(I)$ and

505 refined parameters). CCDC 724802.

Preparation of compound 2

Complex **1** (0.041 g, 0.05 mmol) and 2,2,6,6-tetramethylpiperidine (0.141g, 0.1mmol) were added to a 50 mL Schlenk and dissolved in toluene (5 mL) giving a yellow solution. The solution was filled with H_2 (1500 mbar) and allowed the solution to stir at 80°C for 24 h. There was no precipitation formed during this process. The reaction was then concentrated to half volume and hexane was added to promote precipitation. The product was washed by hexane after filtration and dried *in vacuo*. Yield: 23 %. Crystals were obtained from a mixture of benzene / hexane at 25 °C. Anal.Calcd. for $C_{43}H_{27}B_2F_{20}N$: C, 53.84; H, 2.84; N, 1.46. Found: C, 53.69; H, 2.77; N, 1.39. ^{1}H NMR (benzene-d_6, 200 MHz, 293 K): δ = 7.82 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.51 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.30 (t, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 2.89 (br, 1H, B*H*B), 2.11 (s, 2H, N*H*), 0.66 (m, 2H, CH_2), 0.48 (m, 4H, CH_2), 0.22 ppm (s, 12H, CH_3). ^{19}F NMR (benzene-d_6, 188 MHz, 293 K): δ = -129.8 (d, 8F, $^3J_{FF}$ = 24 Hz, *o*-C_6F_5), -159.6 (t, 4F, $^3J_{FF}$ = 26 Hz, *p*-C_6F_5), -166.3 ppm (t, 8F, *m*-C_6F_5). The solubility of **2** was too low to permit weak (C_6F_5) resonances to be observed in the ^{13}C{^{1}H} NMR spectrum.

X-ray Crystal Structure Analysis of **2**: formula $C_{49}H_{33}B_2F_{20}N$, *M*r = 1037.38, Monoclinic, $P2_1/c$, a = 28.2693(9), b = 16.9611(5), c = 18.6599(9) Å, β = 96.118(3)°, V = 8896.1(6) Å^3, Z = 8, μ = 0.148 mm^{-1}, 74894 reflections collected, 15793 independent (R_{int} = 0.1511), R_1 = 0.0679, wR_2 = 0.1414 (for 6368 observed reflections with $I \geq 2\sigma$ (I) and 1288 refined parameters). CCDC 731638.

Preparation of compound 3

Complex **1** (0.041 g, 0.05 mmol) and Tri-*tert*-butylphosphine (0.02g, 0.1mmol) were added to a 50 mL Schlenk and dissolved in toluene (5 mL) giving a yellow solution. The solution was filled with H_2 (1500 mbar) and allowed the solution to stir at 80°C for 24 h. A little precipitation formed during this process. The reaction was then concentrated to half volume and hexane was added to promote precipitation. The product was washed by hexane after filtration and dried *in vacuo*. Yield: 32 %. Crystals were obtained from a mixture of benzene / hexane at 25 °C. Anal.Calcd. for $C_{46}H_{35}B_2F_{20}P$: C, 54.15; H, 3.46. Found: C, 54.10; H, 3.39.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.60 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.41 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.32 (t, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 4.69 (d, 1H, $^1J_{PH}$ = 430 Hz, P-*H*), 1.40 ppm (d, 27H, $^1J_{PH}$ = 16 Hz, P{C(CH_3)$_3$}$_3$). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ = -130.2 (d, 8F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -161.2 (t, 4F, $^3J_{FF}$ = 24 Hz, *p*-C_6F_5), -167.0 ppm (t, 8F, *m*-C_6F_5). ^{31}P {^{1}H} NMR ($CDCl_3$, 81 MHz, 293 K): δ = 60.7 ppm (s). The solubility of **3** was too low to permit weak (C_6F_5) resonances to be observed in the ^{13}C NMR spectrum.

X-ray Crystal Structure Analysis of **3**: formula $C_{61}H_{50}B_2F_{20}P$, *M*r = 1215.60, Monoclinic, $P2_1/n$, a = 15.7237(3), b = 19.8823(3), c = 17.9932(3) Å, β = 91.391(2)°, V = 5623.44(17) Å^3, Z = 4, μ = 0.155 mm^{-1}, 58618 reflections collected, 10296 independent (R_{int} = 0.0495), R_1 = 0.0502, wR_2 = 0.1155 (for 6268 observed reflections with $I \geq 2\sigma$ (*I*) and 772 refined parameters).

Preparation of compound 4

Complex **1** (0.0082 g, 0.01 mmol) and benzophenone imine (0.0018 g, 0.01 mmol or 0.0036 g, 0.02 mmol) were dissolved in benzene (0.5 mL) giving a yellow solution. The yellow precipitate formed after 5 min at rt. The product was washed by hexane after filtration and dried *in vacuo*. Yield: 65%. Crystals were obtained from a mixture of chloroform/hexane at 25 °C. Anal.Calcd. for $C_{60}H_{28}B_2F_{20}N_2$: C, 61.15; H, 2.39; N, 2.38. Found: C, 61.06; H, 2.31; N, 2.17. ^{1}H NMR (benzene-d_6, 200 MHz, 293K): δ = 10.67 (br, 2H, NH), 7.75 (d, 4H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.23-6.98 (m, 14H, Ar-*H*), 6.52 (t, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.33 (t, 4H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.17 ppm (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*). ^{11}B {^{1}H} NMR (benzene-d_6, 64 MHz, 293 K): δ = -10.4 ppm (s). ^{19}F NMR (benzene-d_6, 188 MHz, 293 K): δ = -127.5 (d, 2F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -130.1 (d, 2F, $^3J_{FF}$ = 26 Hz, *o*-C_6F_5), -137.0 (br, 2F, *o*-C_6F_5), -140.6 (d, 2F, $^3J_{FF}$ = 24 Hz, *o*-C_6F_5), -157.8 (t, 2F, $^3J_{FF}$ = 19 Hz, *p*-C_6F_5), -160.1 (t, 1F, $^3J_{FF}$ = 24 Hz, *p*-C_6F_5), -163.4 (br, 1F, *p*-C_6F_5), -165.5 ppm (m, 8F, *m*-C_6F_5). The solubility of **3** was too low to permit weak (C_6F_5) resonances to be observed in the ^{13}C NMR spectrum.

X-ray Crystal Structure Analysis of **4**: formula $C_{249}H_{129}B_8Cl_9F_{80}N_8$, *M*r = 5158.14, Monoclinic, $P2_1$/n, a = 19.6245(2), b = 24.8943(3), c = 22.7758(3) Å, β = 98.977(1)°, V = 10990.6(2) Å^3, Z = 2, μ = 0.243 mm^{-1}, 113766 reflections collected, 20853 independent (R_{int} =

0.0395), R_1 = 0.0696, wR_2 = 0.1941 (for 13444 observed reflections with $I \geq 2\sigma(I)$ and 1599 refined parameters). CCDC 724803.

Catalytic hydrogenation of imines using Complex 1 or $B(C_6F_5)_3$

1. 5 or 15 bar H_2

A [D]-benzene solution of imines (0.05 mmol) and complex **1** (0.0041g, 0.005mmol) or $B(C_6F_5)_3$ (0.0026g, 0.005mmol) was added to a 25 mL steel autoclave, and filled with (15 or 5) bar H_2. ^{1}H NMR spectra were taken after 1 h of the reaction at 120 ^{o}C.

2. 1500 mbar H_2

In a 25 mL Young Schlenk, a [D]-benzene solution of PhCH=N*t*Bu (0.05 mmol) and complex **1** (0.0041 g, 0.005 mmol) or $B(C_6F_5)_3$ (0.0026 g, 0.005 mmol) were added. After freezing the solution, the N_2 atmosphere was exchanged with 1500 mbar of H_2. The solution was heated at 80 ^{o}C. Monitor the reaction mixture by ^{1}H NMR.

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Supporting information

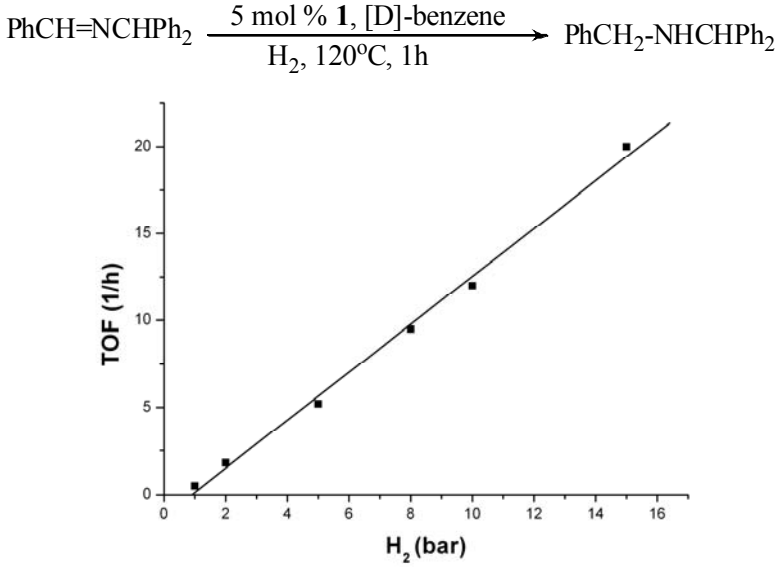
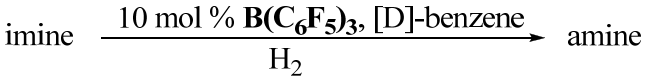


*Figure S1. Catalytic hydrogenation of $PhCH=NCHPh_2$ with **1** at 120 ^oC for 1 h under variation of the H_2 pressure.*

Table S1

Catalytic hydrogenation of imines with $B(C_6F_5)_3$ and H_2.



Entry	Substrate	t (h)	T (^oC)	H_2 (bar)	Product	Yield (%)
1	PhCH=N*t*Bu	1	80	1.5	$PhCH_2NH$*t*Bu	> 99
2	PhCH=N*t*Bu[a)]	12	80	1.5	$PhCH_2NH$*t*Bu	> 99
3	*p*-$ClC_6H_4CH=NC_6H_4Cl$-*p*	1	120	5	*p*-$ClC_6H_4CH_2NHC_6H_4Cl$-*p*	> 99
4	*p*-$ClC_6H_4CH=NC_6H_4Cl$-*p* [a)]	1	120	5	*p*-$ClC_6H_4CH_2NHC_6H_4Cl$-*p*	34

a) Catalyzed by **1**.

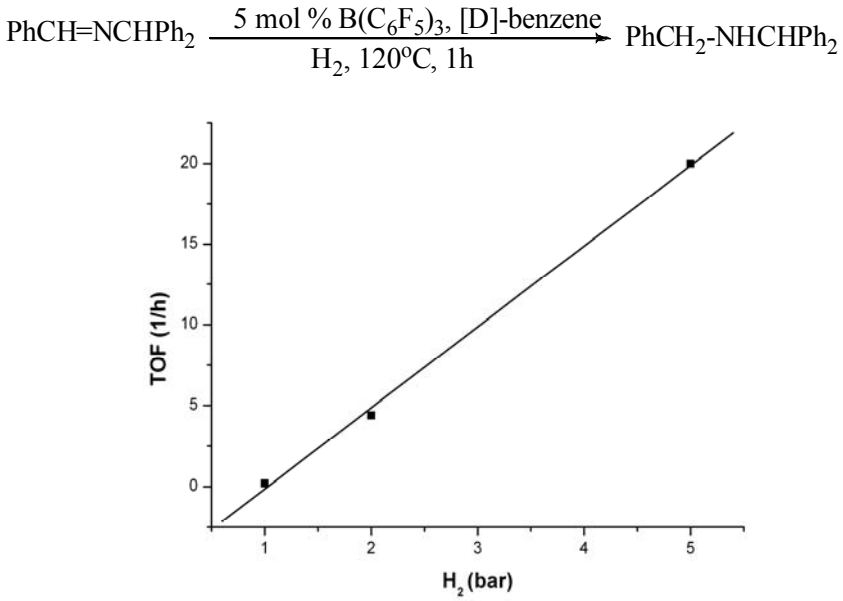


Figure S2. Catalytic hydrogenation of $PhCH=NCHPh_2$ with $B(C_6F_5)_3$ at 120 °C for 1 h under variation of the H_2 pressure.

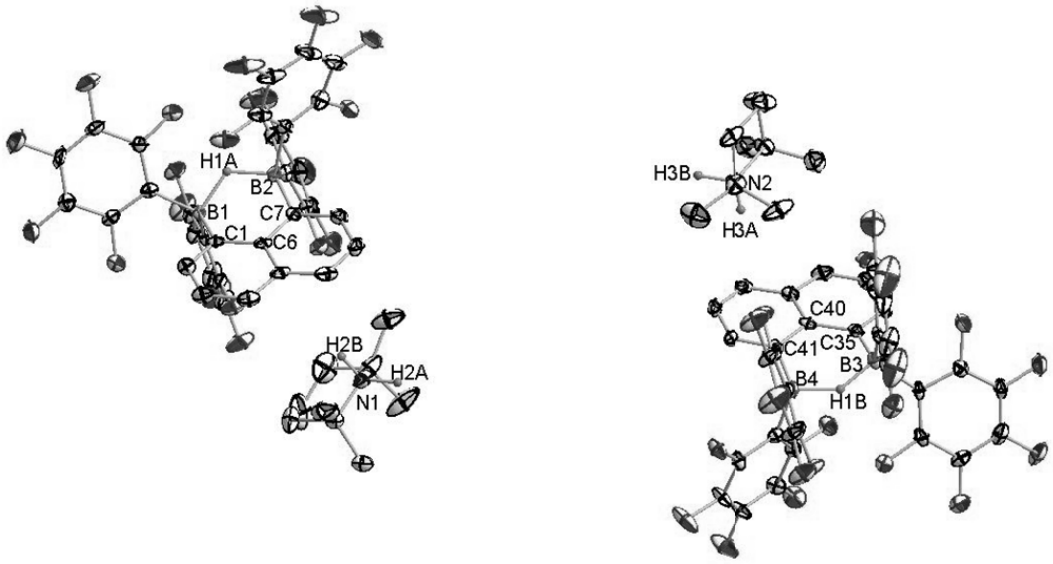


Figure S3. A view of the molecular structure of compound ***2****. Hydrogen atoms except for BH and NH are omitted for clarity.*

Selected bond lengths [Å] and Selected bond angles [°] of compound **2**.

B1-H1A	1.46(4)	B2-H1A	1.41(4)	N1-H2A	0.88(3)
N1-H2B	0.87(4)	B3-H1B	1.32(4)	B4-H1B	1.37(4)
N2-H3A	0.87(3)	N2-H3B	0.88(4)	B1···B2	2.491(8)
B3···B4	2.534(8)	C6-C1-B1	118.5(4)	C6-C7-B2	120.3(5)
C6-C7-B2	120.3(5)	C1-B1-H1A	108.5(16)	C7-B2-H1A	113.0(15)
C1-C6-C7	120.0(4)	C40-C35-B3	119.4(4)	C35-C40-C41	120.0(4)
C40-C41-B4	119.8(4)	C35-B3-H1B	101.0(19)	C41-B4-H1B	104.0(16)

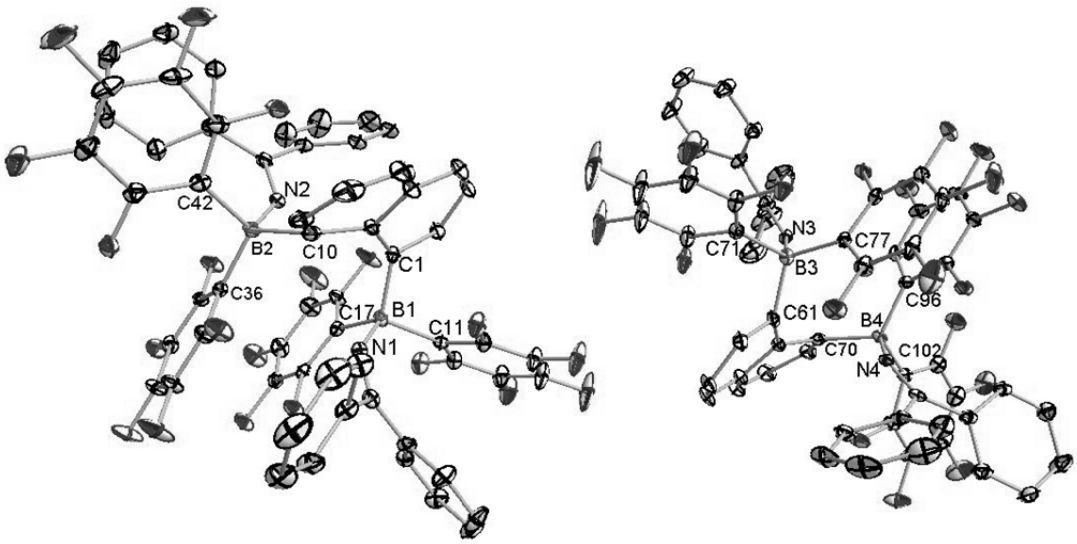


Figure S4. A view of the molecular structure of compound ***4****. Hydrogen atoms are omitted for clarity.*

Selected bond lengths [Å] and Selected bond angles [°] of compound **4**

B1-N1	1.598(4)	B1-C1	1.673(5)	B1-C11	1.657(4)
B1-C17	1.646(4)	B2-N2	1.601(4)	B2-C10	1.678(5)
B2-C36	1.641(4)	B2-C42	1.660(5)	C61-B3	1.674(5)
C71-B3	1.660(5)	C77-B3	1.641(4)	B3-N3	1.600(4)
C70-B4	1.671(5)	C96-B4	1.654(4)	C102-B4	1.662(5)
B4-N4	1.603(4)	B1···B2	3.851(5)	C17-B1-C11	112.0(2)
N1-B1-C17	109.0(2)	N1-B1-C11	107.1(2)	C17-B1-C1	119.1(2)
C17-B1-C11	112.0(2)	N1-B1-C1	103.6(2)	N2-B2-C42	108.4(2)
C11-B1-C1	105.2(2)	N2-B2-C36	108.6(2)	C36-B2-C10	118.5(3)
C36-B2-C42	111.3(2)	N2-B2-C10	103.7(2)	N3-B3-C71	108.4(2)
C42-B2-C10	105.8(2)	N3-B3-C77	110.3(2)	C77-B3-C61	117.8(3)
C77-B3-C71	110.1(2)	N3-B3-C61	103.4(2)	C71-B3-C61	106.4(2)

Metal-Free Hydrogen Activation by the Frustrated Lewis Pairs of $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ and Bulky Lewis Bases

Abstract

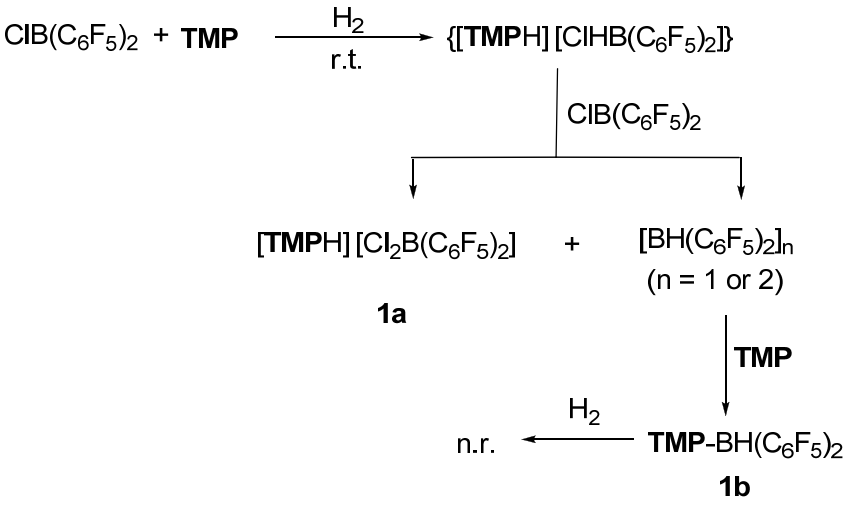
The frustrated Lewis pair (FLP) derived from $ClB(C_6F_5)_2$ and the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), tri-*tert*-butylphosphine, tris(2,4,6-trimethylphenyl) phosphine, cleaved H_2 heterolytically to form the intermediate anion $[HClB(C_6F_5)_2]^-$, which quickly underwent hydride/chloride exchange with the remaining $ClB(C_6F_5)_2$ to give the known compound $[HB(C_6F_5)_2]_n$ (n = 1 or 2) and the anion $[Cl_2B(C_6F_5)_2]^-$ present in the products [**TMP**H][$Cl_2B(C_6F_5)_2$] **1a**, [tBu$_3$PH][$Cl_2B(C_6F_5)_2$] **2a**, [Mes$_3$PH][$Cl_2B(C_6F_5)_2$] **3a**. $[HB(C_6F_5)_2]_n$ forms Lewis adducts with **TMP** and tBu$_3$P: **TMP**-$BH(C_6F_5)_2$ **1b** and tBu$_3$P-$BH(C_6F_5)_2$ **2b**. The Lewis adduct tBu$_3$P-$BH(C_6F_5)_2$ was found capable of generating a FLP at elevated temperature and was reacted with H_2 producing the splitting product [tBu$_3$PH][$H_2B(C_6F_5)_2$] **2c**. Mes$_3$P forms no Lewis adduct with $[HB(C_6F_5)_2]_n$, but a FLP, which was also capable of splitting H_2 to yield initially [Mes$_3$PH][$H_2B(C_6F_5)_2$]. The $[H_2B(C_6F_5)_2]^-$ anion underwent disproportionation to form [Mes$_3$PH][$HB(C_6F_5)_3$] **3b**, Mes$_3$P, $[H_2B(C_6F_5)]_2$ and H_2. Similarly, 2,4,6-tri-*tert*-butylpyridine (**TTBP**) and $[HB(C_6F_5)_2]_n$ gave in the presence of H_2 the final products [**TTBP**H][$HB(C_6F_5)_3$] salt and $[H_2B(C_6F_5)]_2$. The contrasting reactivities of the tBu$_3$P/$[BH(C_6F_5)_2]_n$ and the Mes$_3$P/$[HB(C_6F_5)_2]_n$ and the **TTBP**/$[HB(C_6F_5)_2]_n$ pairs were explained on the basis of the different pK_a's of the $[LBH]^+$ cations. After disproportionation of the $[H_2B(C_6F_5)_2]^-$ anion to give [Mes$_3$PH][$HB(C_6F_5)_3$] **3b** or [**TTBP**H][$HB(C_6F_5)_3$] **4a,** the also formed $[H_3B(C_6F_5)]^-$ anion reacted with the more acidic cations ($[Mes_3PH]^+$, [**TTBP**H]$^+$) to give H_2 and *syn* and *anti* $[H_2B(C_6F_5)]_2$ **3c**. **1a**, **2a**, **3a** and **4a** were studied by single crystal X-ray diffraction analysis.

Introduction

The concept of frustrated Lewis pairs (FLPs) was put forward by D. W. Stephan et al in 2006 after their remarkable discovery that H_2 can reversibly be activated by the "metal-free" compound $[(2,4,6\text{-}C_6H_2Me_3)_2P(H)(C_6F_5)B(H)\text{-}(C_6F_5)_2]$.[1] As one of the fruitful applications of this concept, "metal-free" catalysts could be developed for the hydrogenation of bulky imines.[2] In such systems sterically hindered Lewis donors and acceptors are combined to establish encounter complexes. Their steric congestion precludes the formation of classical Lewis adducts and their relative close proximity indeed provokes H_2 activation, but also "unquenched" reactivity towards small molecules.[3,4] For instance, the mixtures of frustrated phosphine and borane pairs can activate H_2 heterolytically under very mild condition,[5] but can undergo addition of olefins, as well.[6,7] Similarily following their pioneering work an increasing number of related "FLPs" were created, which were on the one hand capable of activating H_2 heterolytically, but on the other hand also other small molecules.[8-17] Some of the zwitterionic products resulting from H_2 splitting were shown to serve as active catalysts for the hydrogenation of imines, nitriles and aziridines, as well as enamine and C=C double bonds of enol silyl ether.[18-20] Presently FLP formation is no longer limited to boron/phosphine systems, since Stephan et al and Tamm et al extended the range of FLPs to boron/carbene combinations, in which for H_2 activation the steric demands of the Lewis pair constituents are very crucial to their reactivity.[9,10] For the same purpose Rieger et al introduced the borane/amine variant for FLPs.[11] The majority of Lewis acids used were trispentafluorophenylborane, $B(C_6F_5)_3$, or closely related molecules. The $ClB(C_6F_5)_2$, $HB(C_6F_5)_2$ compounds were chosen to act as a highly active hydroboration reagents or as synthons for the incorporation of Lewis acidic $-B(C_6F_5)_2$ groups into molecular frameworks building new intramolecular FLPs.[8,13,18,19] However, as yet these compounds have not been used as Lewis acidic components in FLPs to activate H_2. We therefore tried to approach utilization of the "robust" molecules $ClB(C_6F_5)_2$[21] and $HB(C_6F_5)_2$[22] in FLPs together with 2,2,6,6-tetramethylpiperidine (**TMP**) or phosphines R_3P (R = *t*-Bu, 2,4,6-trimethylphenyl = Mes) for cleavage of H_2.

Results and Discussion

Toluene solutions of stoichiometric mixtures of 2,2,6,6-tetramethylpiperidine (**TMP**) or of the sterically hindered phosphines R_3P (R = *t*-Bu, 2,4,6-trimethylphenyl) and $ClB(C_6F_5)_2$ were at first explored for Lewis adduct formation by ^1H, ^{19}F, ^{11}B NMR spectroscopy. We found only unchanged signals due to the free starting materials and no hint of Lewis adduct formation by these sterically quite congested molecules. We can, however, suppose that contact pairs, the FLPs, had formed, since, for instance, exposure of a **TMP**/$ClB(C_6F_5)_2$ toluene solution to an atmosphere of H_2 (1000 mbar) induced a reaction proceeding at ambient temperature. Initial formation of [**TMP**H][$ClHB(C_6F_5)_2$] is assumed, but this species is not stable in the presence of $ClB(C_6F_5)_2$ and is transformed subsequently into the [**TMP**H][$Cl_2B(C_6F_5)_2$] salt **1a**. The chloride/hydride metathesis also produces the known equilibrium mixture of the monomeric and dimeric borohydride $[HB(C_6F_5)_2]_n$ (n = 1,2)[23] (Scheme 3.1). $[HB(C_6F_5)_2]_n$ quickly associates with the remaining **TMP** to afford the stable Lewis acid-base adduct **TMP**-$BH(C_6F_5)_2$ **1b**. **1b**, which apparently is such a tight adduct that FLP reactivity towards H_2 could not be initiated even at elevated temperatures (Scheme 3.1). The formation of **1a** and **1b** according to Scheme 3.1 could be analyzed by ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of the reaction mixture (spectrum A) and its



Scheme 3.1

assignments are shown in Figure 3.1 in comparison with spectra of pure **1a** (B) and **1b** (C). **1a** could be isolated from the reaction mixture as a white solid in *ca.* 35 % yield. The ^{1}H NMR spectrum of **1a** features a broad NH_2 resonance at 5.90 ppm, and the ^{19}F NMR spectrum shows signals at δ -134.6 (*o*-), -163.9 (*p*-), -167.3 ppm (*m*-C_6F_5) consistent with the four-coordinate boron atom of the anion ($\Delta\delta_{m,p}$ = 3.4). The X-ray diffraction study of **1a** (Figure 3.2) reveals an overall centrosymmetric chair form of pairs of **1a** held together by hydrogen bonding. Each boron atom is connected to two chlorine atoms and two C_6F_5 groups in tetrahedral environment. The N1-H1 and N1-H2 distances are 0.90(2) and 0.85(2) Å, and the H1-N1-H2 angle is 104.7(2)°. The Cl1-B1-Cl2 angle is 105.42(8)° and the B-Cl bonds possess an average length of 1.89 Å. Intermolecular N-H···Cl hydrogen bonds link the pairs of ions with H1···Cl1 and H2···Cl2^i separations of 2.50(2) and 2.47(2) Å, respectively.

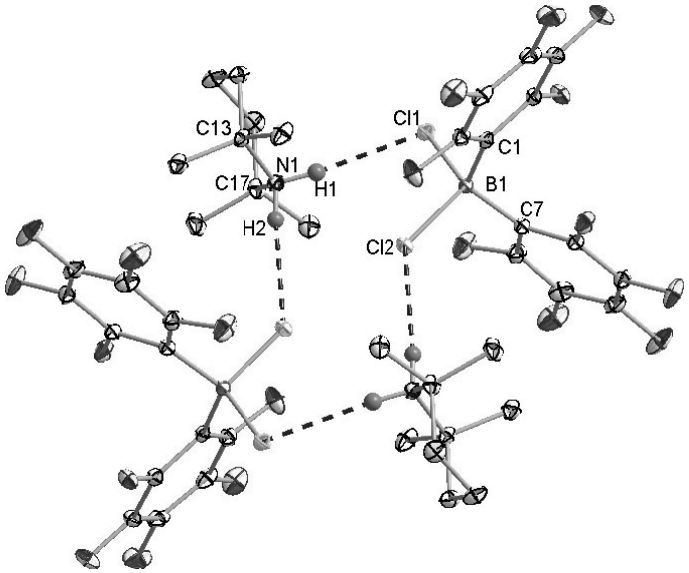


Figure 3.2 Molecular structure of ***1a****. Hydrogen atoms except for the H_N atom are omitted for clarity.*

Pure **1b** was prepared from the reaction of a stoichiometric mixture of $[HB(C_6F_5)_2]_n$ (n = 1 or 2) and **TMP** obtained as a white solid in 86 % yield. In the ^{1}H NMR spectrum **1b** features a broad H_B resonance at 4.18 ppm, and the ^{11}B NMR resonance is located at δ -11.8 ppm. The ^{19}F NMR spectrum provides furthermore evidence for the inequivalence of the phenyl rings, since two sets of signals are attributable to the *ortho*- (δ -131.2, -135.1 ppm) and

meta-fluorine atoms (δ-165.6, -166.9 ppm),but just one signal is found for the *para*-fluorine atoms (δ -160.0 ppm). This observation suggests hindered rotation of the C_6F_5 rings around the B-C bonds, which presumably arises from steric contacts between the methyl substituents of the piperidine moiety and the fluorine atoms or forms $H_{TMP}\cdots F$ hydrogen bonding.

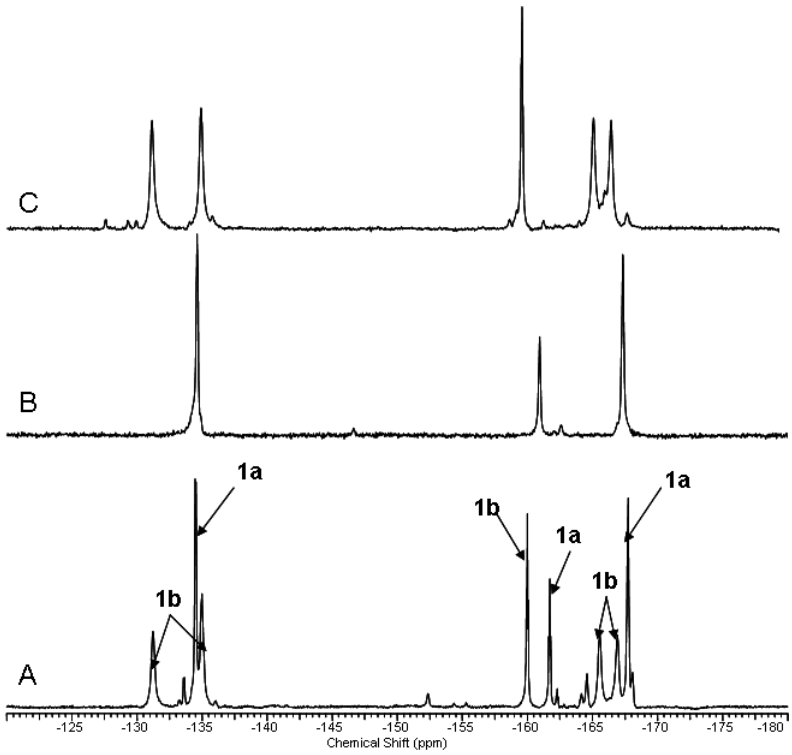
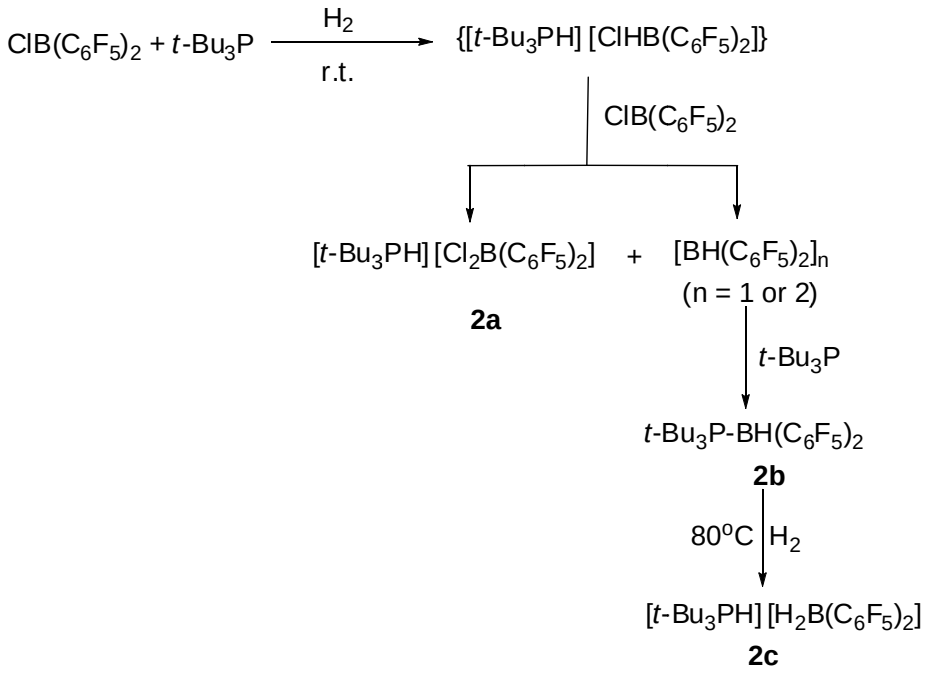


Figure 3.1 ***A****: ^{19}F NMR spectra of the mixture of* ***TMP****-$ClB(C_6F_5)_2$ with H_2 after ca. 30 min in toluene-d_8;* ***B*** *and* ***C****: ^{19}F NMR spectra of pure* ***1a*** *and* ***1b*** *in toluene-d_8.*

Similar to the reaction with **TMP**, the phosphines *t*-Bu_3P and Mes_3P (Mes = 2,4,6-trimethylphenyl) were reacted with $ClB(C_6F_5)_2$ under an atmosphere of H_2 to yield initially salts of the phosphonium ions with the unstable $[ClHB(C_6F_5)_2]^-$ anion (Schemes 3.2 and 3.3). As for the **TMP** reaction, this anion then undergoes fast hydride/chloride exchange with $ClB(C_6F_5)_2$ to generate the $[Cl_2B(C_6F_5)_2]^-$ anion and the equilibrium mixture of the monomeric and dimeric hydrides $[HB(C_6F_5)_2]_n$ (n = 1 or 2). The products thus were [*t*-Bu_3PH][$Cl_2B(C_6F_5)_2$] **2a** and [Mes_3PH][$Cl_2B(C_6F_5)_2$] **3a**, which exhibit ^{19}F and ^{11}B NMR spectra similar to those resonances seen for the $[Cl_2B(C_6F_5)_2]^-$ anion of **1a**. The cations of **2a** and **3a** show ^{31}P NMR resonances at 51.8 and -25.7 ppm with typically large *J*(P,H) coupling



Scheme 3.2

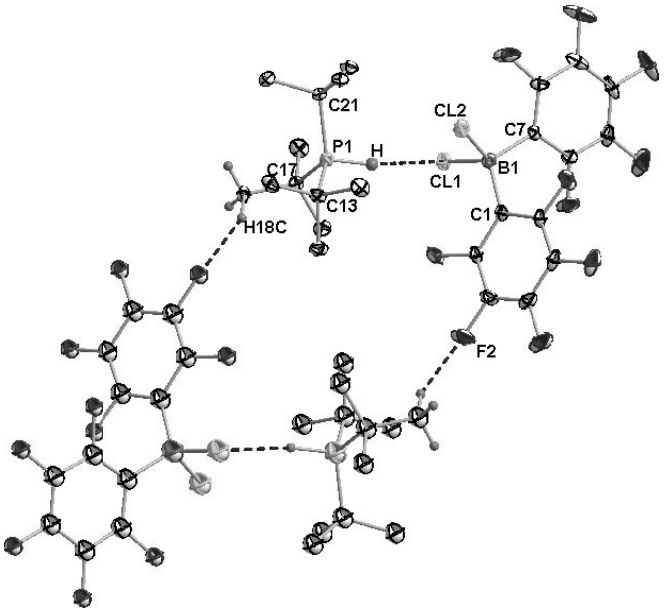


Figure 3.3 Molecular structure of **2a**. *Hydrogen atoms except for the H_P and H_{C18} atoms are omitted for clarity.*

constants of 440 and 472 Hz, respectively. The ^{1}H NMR signals of the H_P protons are found at δ 5.12 (**2a**) and 8.48 ppm (**3a**). A crystallographic study of **2a** reveals a square-type

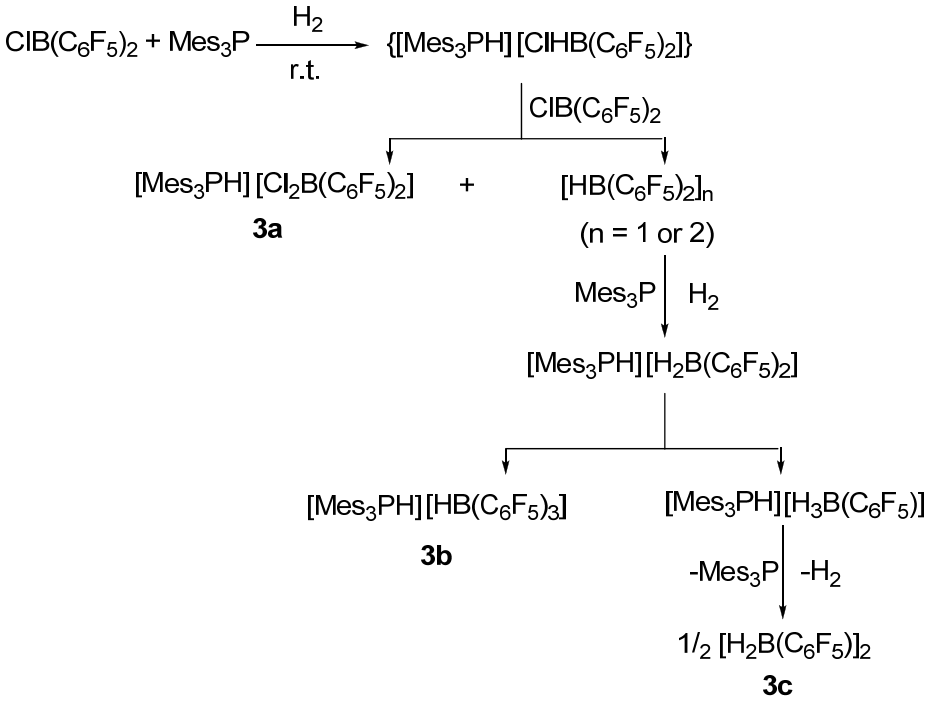
structure similar to **1a** (Figure 3.3). The ions are connected through weak P-H···Cl and C-H···F hydrogen bonds with H···Cl1 distance of 2.78(2) and H18C···F2A of 2.54 Å. The P-H distance is 1.30(2) Å, and the Cl1-B1-Cl2 angle and the Cl-B distance are quite close to those of **1a**. Strong hydrogen bonding could not be traced in the structure of **3a**, the Cl2···H1 distance amounts to 2.95 Å, which is significantly longer than the corresponding interactions in **1a** (2.50(2) Å) and **2a** (2.47(2) Å) (Figure 3.4). The Cl1-B1-Cl2 angle and the Cl-B distance of **3a** are comparable to those of **2a**.

The equilibrium mixture of $[HB(C_6F_5)_2]_n$ formed initially according to Schemes 3.2 and 3.3 reacted differently with *t*-Bu_3P and Mes_3P. *t*-Bu_3P produced the isolable Lewis adduct *t*Bu_3P-$BH(C_6F_5)_2$ **2b**. **2b** could independently be prepared from a stoichiometric mixture of $[HB(C_6F_5)_2]_n$ and *t*-Bu_3P in toluene. In the ^{19}F NMR spectrum it is characterized by a set of signals at δ -124.6 (*o*-), -158.9 (*p*-), -164.2 ppm (*m*-C_6F_5). The ^{31}P NMR signal of this adduct is found at δ 47.6 ppm and the ^{11}B NMR resonance is at -27.4 ppm, which is consistent with the tetrahedral boron center of **2b**. Interestingly, upon a raise in temperature to 80 °C, **2b** reacted further with H_2 affording the isolable ionic species [*t*Bu_3PH][$H_2B(C_6F_5)_2$] **2c**. The elevated temperature apparently promotes dissociation of the Lewis adduct to form a FLP.

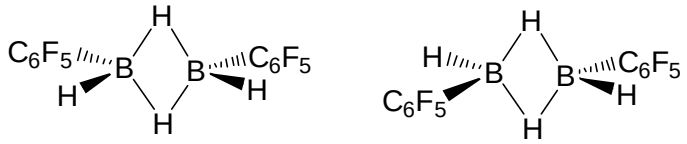
The relative stability of **2c** is mainly attributed to the stability of the anion in the presence of the [*t*Bu_3PH]$^+$ cation displaying too low acidity[24] for further transformation like the salt of this anion with the [Mes_3PH]$^+$ cation (*vide infra* Scheme 3.3). The ^1H and ^{31}P NMR spectra of **2c** exhibited the expected resonances. The ^{11}B NMR spectrum shows a triplet at -30.2 ppm with a B-H coupling constant of 90 Hz and the corresponding ^1H NMR resonance is found at 3.01 ppm (q, br, B-H). Moreover, the $\Delta\delta$ (*m*-F)-(*p*-F) separation is consistent with the presence of an anionic four-coordinate boron atom.

Toluene solutions of stoichiometric mixtures of Mes_3P and $[HB(C_6F_5)_2]_n$ did not lead to formation of a Lewis adduct. The mixture was however found to act as a FLP capable of splitting H_2 heterolytically under ambient conditions and generate - somewhat unexpected - the [Mes_3PH][$HB(C_6F_5)_3$] salt **3b** as one of the final products. Compound **3b** possesses the following ^1H NMR data: δ 7.93 ppm (d, $^1J_{P\text{-}H}$ = 460 Hz), ^{11}B NMR: δ -20.2 ppm (d, $J_{B\text{-}H}$ = 82 Hz) and ^{19}F NMR resonances: δ -133.7, -164.6, -168.3 ppm after exposure of the toluene

solution of Mes_3P-$[HB(C_6F_5)_2]_n$ at H_2 atmosphere for 30 min. Another ^{11}B NMR resonance at 9.5 ppm (br) and a set of ^{19}F NMR signals at δ -136.8, -137.5, -160.7, -162.1, -166.2 and -166.6 ppm were additionally recognized in the spectra of the reaction solution.



Scheme 3.3



syn **3c** *anti*

These signals were attributed to the *syn* and *anti* isomers of $[H_2B(C_6F_5)]_2$ **3c** formed via disproportionation of the $[H_2B(C_6F_5)_2]^-$anion.[25] But the *syn*-$[H_2B(C_6F_5)]_2$ (^{19}F NMR signals at δ -136.8, -162.1, -166.6 ppm) was not stable in solution which was completely converted after several hours into *anti*-$[H_2B(C_6F_5)]_2$ **3c** (^{19}F NMR signals at δ -137.5, -160.7, -166.2 ppm). The ^1H NMR spectrum of **3c** was less informative, since resonances for the hydride substituents (terminal or bridging) could not be detected. This was explained on the basis of a

broadening of these resonances due to the direct neighbourhood with the ^{11}B quadrupole nuclei.

Selected bond lengths [Å] and Selected bond angles [°] of compound **1a** and **2a**.

Compound 1a					
N1-H1	0.90(2)	H1···Cl1	2.50(2)	N1-H2	0.85(2)
H2···Cl2^{i}	2.47(2)	N1-C13	1.532(2)	N1-C17	1.529(2)
B1-Cl1	1.905(2)	B1-Cl2	1.885(2)	B1-C1	1.618(2)
B1-C7	1.623(2)	H1-N1-H2	104.7(2)	H1-N1-C17	105.1(1)
H1-N1-C13	107.9(1)	H2-N1-C13	108.7(1)	H2-N1-C17	108.7(1)
C13-N1-C17	120.8(1)	Cl1-B-Cl2	105.42(8)	Cl2-B1-C1	113.89(1)
Cl2-B1-C7	104.57(9)	C1-B1-C7	115.92(1)	Cl1-B1-C7	111.8(1)
Cl1-B1-C1	104.95(9)	N1-H1···Cl1	174.8(15)	N2-H2···Cl2^{i}	173.6(15)
Symmetry transformation (i) used to generate equivalent atoms: 1-x, 1-y, -z.					
Compound 2a					
P1-H	1.30(2)	H···Cl1	2.78(2)	H18C···F2^{i}	2.54
P1-C21	1.869(2)	P1-C17	1.867(2)	P1-C13	1.871(2)
B1-Cl1	1.891(2)	B1-Cl2	1.895(2)	B1-C1	1.625(2)
B1-C7	1.630(2)	C21-P1-H	103.7(7)	C13-P1-H	104.3(7)
C17-P1-H	104.1(6)	C21-P-C17	114.72(7)	C17-P1-C13	113.95(7)
C21-P1-C13	114.26(8)	Cl1-B-Cl2	107.64(9)	Cl1-B1-C1	113.8(1)
Cl1-B1-C7	114.1(1)	C1-B1-C7	114.3(1)	Cl2-B1-C7	113.28(1)
Cl2-B1-C1	103.8(1)	P1-H···Cl1	148.1(9)	C18-H18C···	F2^{i} 156
Symmetry transformation (i) used to generate equivalent atoms: -x, -y,1-z.					

Mes_3P can not form a stable Mes_3P-$BH(C_6F_5)_2$ Lewis adduct, but a reactive $Mes_3P\cdots BH(C_6F_5)_2$ FLP, since reactivity similar to that of the tBu$_3$P···$BH(C_6F_5)_2$ FLP was found. The $Mes_3P\cdots BH(C_6F_5)_2$ encounter complex can apparently split H_2 to initially generate the $[H_2B(C_6F_5)_2]^-$ anion which can be detected via ^{11}B NMR as a transient during the reaction process. As a subsequent reaction step disproportionation of this anion occurs producing in equilibrium the substituent exchange products $[HB(C_6F_5)_3]^-$ and $[H_3B(C_6F_5)]^-$[26] (Scheme 3.3). The quite basic $[H_3B(C_6F_5)]^-$ anion is quickly withdrawn from equilibrium via the acid-base reaction with the acidic $[Mes_3PH]^+$ cation evolving H_2 and forming $[H_2B(C_6F_5)]_2$

(Scheme 3.3). It should be mentioned at this point that the $[H_2B(C_6F_5)_2]^-$ anion of **2c** is also believed to undergo this disproportionation process. The disproportionation occur for the $[H_2B(C_6F_5)_2]^-$ anions of both salts $[t\text{Bu}_3\text{PH}][H_2B(C_6F_5)_2]$, $[\text{Mes}_3\text{PH}][H_2B(C_6F_5)_2]$ (Schemes 3.2 and 3.3), however with low actual equilibrium concentrations of the $[H_3B(C_6F_5)]^-$ anion, too low to enable acid-base reaction with the less acidic $[t\text{Bu}_3\text{PH}]^+$ cation, but sufficient for the reaction with the more acidic $[\text{Mes}_3\text{PH}]^+$ cation.[24]

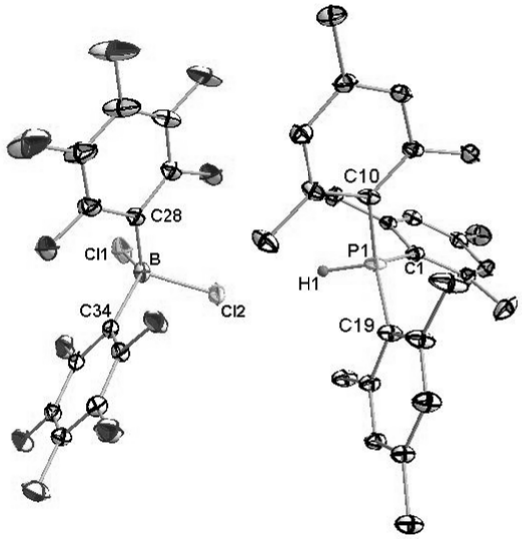


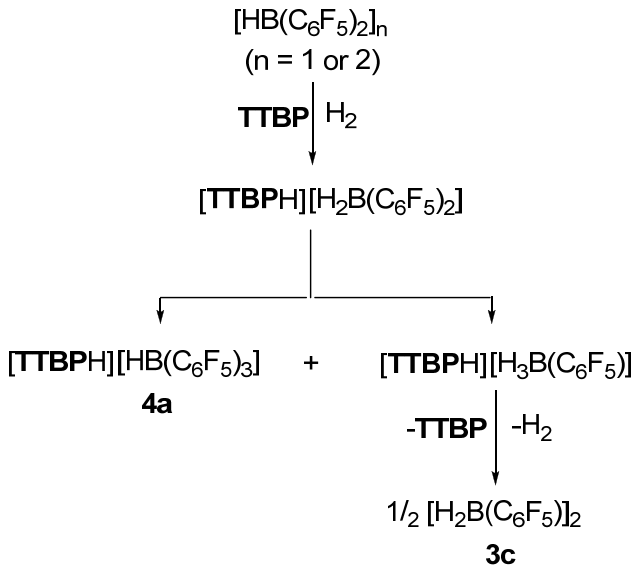
*Figure 3.4 Molecular structure of **3a**. Hydrogen atoms except for the H_P atom are omitted for clarity.*

In order to acquire more information about this H_2 splitting reaction with $[HB(C_6F_5)_2]_n$, the bulky Lewis base 2,4,6-tri-*tert*-butylpyridine (**TTBP**) was applied. **TTBP** was considered to behave similar to Mes_3P, since its protonated form possesses a pK_a similar to that of the $[\text{Mes}_3\text{PH}]^+$ cation[24] and in addition the sterically congested **TTPB** was expected to form a FLP with $[HB(C_6F_5)_2]_n$. Indeed, the reaction of the **TTBP**/$[HB(C_6F_5)_2]_n$ pair with H_2 led to split of this molecule, but also to subsequent disproportionation of the [**TTBP**H][$H_2B(C_6F_5)_2$] salt to afford the stable [**TTBP**H][$HB(C_6F_5)_3$] compound **4a** and the *syn* and *anti* mixture of **3c** (Scheme 3.4). **4a** features the same ^1H, ^{11}B, ^{19}F NMR resonances as the anion of **3b**, but also as a compound prepared independently from $B(C_6F_5)_3$ and **TTBP** with H_2. Crystals grown from the crude mixture allowed a X-ray crystallographic study of **4a** (Figure 3.5),

which showed that the B-H and N-H units are oriented towards each other with a BH···HN non-bonding distance of 3.51(1) Å, which is much longer than that of other related intermolecular dihydrogen bonding separations.

Selected bond lengths [Å] and Selected bond angles [°] of **3a** and **4a**.

Compound 3a					
P1-H1	1.30(1)	P1-C1	1.80(1)	P1-C10	1.80(1)
P1-C19	1.81(1)	B-Cl1	1.86 (2)	B-Cl2	1.93(2)
B1-C28	1.626(2)	B1-C34	1.631(2)	C1-P1-C10	114.05(6)
C1-P1-C19	115.73(6)	C10-P1-C19	115.80(6)	C1-P1-H1	103.4(6)
C10-P1-H1	102.8(6)	C19-P1-H1	102.4(6)	Cl1-B-Cl2	107.43(8)
Cl2-B-C34	102.99(1)	Cl2-B-C28	110.4(1)	Cl1-B-C34	114.1(1)
Cl1-B-C28	105.9(1)	C28-B-C34	115.8(1)		
Compound 4a					
B1-H1	1.15(3)	B1-C7	1.636(4)	B1-C13	1.637(4)
B1-C1	1.648(4)	N1-H1	0.96(3)	N1-C23	1.363(3)
N1-C19	1.354(3)	C7-B1-H1	107.0(2)	C1-B1-H1	103.7(1)
C13-B1-H1	108.6(1)	C7-B1-C13	112.6(2)	C7-B1-C1	114.4(2)
C13-B1-C1	110.0(2)	H2-N1-C23	115.9(2)	H2-N1-C19	119.9(2)
C19-N1-C23	124.3 (3)				



Scheme 3.4

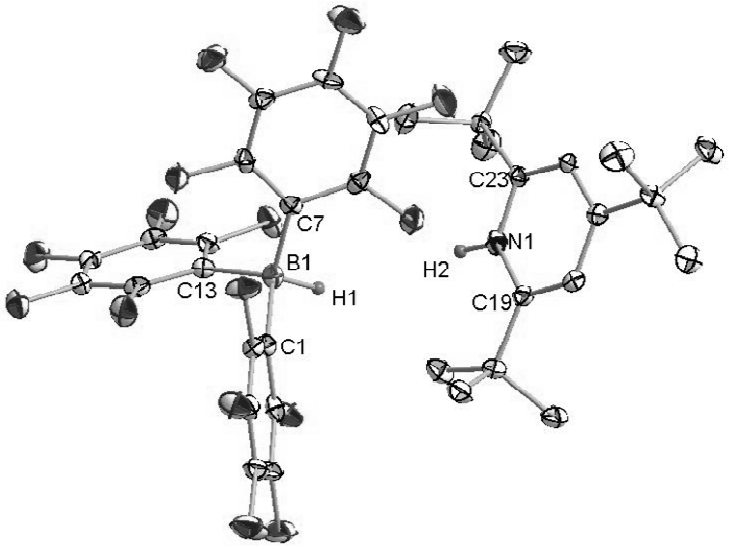


Figure 3.5 Molecular structure of ***4a****. Hydrogen atoms except for the H_N and H_B atoms are omitted for clarity.*

In continuation of these investigations, reduction of imines was probed using $HB(C_6F_5)_2$ or $[t\text{Bu}_3\text{PH}][H_2B(C_6F_5)_2]$ as catalysts. However, in many cases of the applied imines, the formation of too stable amine-boron adducts prevented the formation of FLPs and consequently also catalytic activity. As a result, only PhCH=N*t*Bu could be reduced to the corresponding amine in 95 % yield at 120 °C in the presence of 10 % $HB(C_6F_5)_2$ at a hydrogen pressure of 1300 mbar within 24 h. For the sterically less hindered imines PhCH=NPh and $PhCH=NCHPh_2$ the conversions were usually less than 50 % under the same conditions as mentioned before. This observation supports the idea that FLP formation is crucial to metal-free hydrogenation catalysis and anything precluding such a step leads to suppression of catalysis.

Conclusion

In summary, $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ were employed as Lewis acids (LAs) in FLP chemistry heterolytic splitting of H_2 was observed in the presence of the bulky Lewis bases (LBs) **TMP**, $t\text{Bu}_3\text{P}$, Mes_3P and **TTBP**. The bulkiness of the LB components, the stability of the $[LAH]^-$ anions toward substituent exchanges and the acidities of the $[LBH]^+$ cations were

decisive parameters determining the courses of the reactions following the initial H_2 splitting. On the LB side the $[LBH]^+$ cations $[\mathbf{TMP}H]^+$, $[t\mathrm{Bu_3PH}]^+$, $[\mathrm{Mes_3PH}]^+$, $[\mathbf{TTBP}H]^+$ were formed and the more acidic ones caused follow-up reactions. On the LA side the initially formed $[LAH]^-$ anions were subjected to different reaction courses depending on the mentioned parameters. The $[ClHB(C_6F_5)_2]^-$ anions initially formed from $ClB(C_6F_5)_2$ underwent hydride/chloride exchange with $ClB(C_6F_5)_2$ to give $[Cl_2B(C_6F_5)_2]^-$ and $[HB(C_6F_5)_2]_n$ (n = 1 or 2). **TMP** and $[HB(C_6F_5)_2]_n$ (n = 1 or 2) formed a tight Lewis adduct, unreactive toward H_2. At higher temperatures the Lewis adduct $t\mathrm{Bu_3P\text{-}BH(C_6F_5)_2}$ reacted in form of its $t\mathrm{Bu_3P\cdots BH(C_6F_5)_2}$ FLP with H_2 to generate the salt $[t\mathrm{Bu_3PH}][H_2B(C_6F_5)_2]$. The FLP's $\mathrm{Mes_3P\cdots[HB(C_6F_5)_2]}$ and $\mathbf{TTBP}\cdots[HB(C_6F_5)_2]$ effected formation of the $[H_2B(C_6F_5)_2]^-$ anion as a first intermediate, which then underwent disproportionation of the substituents to form $[\mathrm{Mes_3PH}][HB(C_6F_5)_3]$ or $[\mathbf{TTBP}H][HB(C_6F_5)_3]$ and the quite basic $[H_3B(C_6F_5)]^-$ anion. Unlike $[t\mathrm{Bu_3PH}][H_2B(C_6F_5)_2]$, where the anticipated equilibrium formation of the $[H_3B(C_6F_5)]^-$ anion did not lead to a subsequent acid-base reaction with the $[t\mathrm{Bu_3PH}]^+$ cation, the $[H_3B(C_6F_5)]^-$ anion was withdrawn from the disproportionation equilibrium with the more acidic $[\mathrm{Mes_3PH}]^+$ and $[\mathbf{TTBP}H]^+$ cations affording H_2, LB and *syn* and *anti* $[H_2B(C_6F_5)]_2$.

Experimental part

General consideration: All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze-thaw cycles prior to use. All organic reagents were purchased from Aldrich and used without further purification. $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ were prepared according to the literature.[21,22] ^1H NMR, ^{19}F NMR, $^{11}B\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR data were recorded on a Varian Gemini-200 and 300 spectrometer. Chemical shift are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F, ^{11}B, ^{31}P NMR were referenced to $CFCl_3$, $BF_3\cdot OEt_2$, 85% H_3PO_4, respectively. Microanalyses were carried out at

the Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoKα radiation, λ = 0.71073 Å).[27] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction[28] and data reduction were performed with the Oxford program suite *CrysAlisPro*.[29] The structures were solved with the direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[30] All programs used during the crystal structure determination process are included in the WINGX software.[31] The program PLATON[32] was used to check the results of the X-ray studies and to analyze the hydrogen-bonding systems. The hydrogen atoms bound to nitrogen or phosphorus were located in a difference Fourier map and refined without restraints. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C-H distances in the range 0.93 – 0.97 Å and their isotropic displacement parameters constrained to 1.2U_{eq}(C) or 1.5U_{eq}(C).

Preparation of [TMPH][$Cl_2B(C_6F_5)_2$] 1a

$ClB(C_6F_5)_2$ (0.076 g, 0.2 mmol) and 2,2,6,6-tetramethyl piperidine (**TMP**) (0.0283 g, 0.2 mmol) dissolved in 5 mL of toluene giving a colorless solution. The reaction vessel was filled with H_2 (1000 mbar) and the solution was stirred at room temperature for 4 h. The reaction mixture was then concentrated to half of its volume and hexane was added to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. **1a** was collected as a white solid. Yield: 35 %. Anal. Calcd for $C_{21}H_{20}BCl_2F_{10}N$: C, 45.19; H, 3.61; N, 2.51. Found: C, 45.12; H, 3.63; N, 2.49. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 5.90 (br, 2H, N-H), 0.91 ppm (m, overlap, 18H, TMP-C*H*). ^{11}B{^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ -1.7 ppm (br). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ -134.6 (d, 4F, $^3J_{F\text{-}F}$ = 25 Hz, *o*-C_6F_5), -160.9 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -167.3 ppm (t, 4F, $^3J_{F\text{-}F}$ = 23 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 148.3 (dm, $^1J_{C\text{-}F}$ = 258 Hz, *o*-C_6F_5), 140.5 (dm,

$^1J_{C\text{-}F}$ = 263 Hz, *p*-C_6F_5), 138.2 (dm, $^1J_{C\text{-}F}$ = 262 Hz, *m*-C_6F_5), 59.2 (*o*-C_5H_7N), 34.4 (*m*-C_5H_7N), 26.9 (CH_3), 15.5 ppm (*p*-C_5H_7N). X-ray quality crystals were obtained from a mixture of toluene / hexane at 25°C.

X-ray Crystal Structure Analysis of **1a**: formular $C_{21}H_{20}BCl_2F_{10}N$, *M*r = 558.09, Monoclinic, $P2_1/c$, a = 12.0763(2), b = 11.2761(2), c = 18.3912(3) Å, β = 108.351(2)°, V = 2377.04(7) Å^3, Z = 4, D_c = 1.559 g cm^{-1}, μ = 0.362 mm^{-1}, λ = 0.71073 Å, T = 183(2) K, 23392 reflections collected, 4844 independent [$R_{(int)}$ = 0.0309] and 4150 observed reflections [$I > 2\sigma(I)$], 328 refined parameters, R = 0.0298, wR_2 = 0.0796. CCDC 736257 .

Preparation of TMP-$BH(C_6F_5)_2$ 1b

$HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and 2,2,6,6-tetramethyl piperidine (**TMP**) (0.0283 g, 0.2 mmol) were dissolved in 2 mL of toluene and the colorless solution was stirred at room temperature for 30 mins. The solvent was then removed to half of its original volume *in vacuo*. Hexane was added to induce precipitation, the product was collected as a white solid. Yield: 86 %. Anal. Calcd for $C_{21}H_{20}BF_{10}N$: C, 51.77; H, 4.14; N, 2.88. Found: C, 51.69; H, 4.22; N, 2.95. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 4.18 (s, 1H, B-H), 1.16 (m, 2H, -CH_2), 0.96 (s, 6H, -CH_3), 0.87 (m, overlap, 4H, -CH_2), 0.82 (s, 6H, -CH_3), 0.73 ppm (s, 1H, N-H). ^{11}B{^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ -11.8 ppm (br). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ -131.2 (s, 2F, *o*-C_6F_5), -135.1 (s, 2F, *o*-C_6F_5), -160.0 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -165.6 (s, 2F, *m*-C_6F_5), -166.9 ppm (s, 2F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 149.6 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *o*-C_6F_5), 140.5 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *p*-C_6F_5), 137.9 (dm, $^1J_{C\text{-}F}$ = 241 Hz, *m*-C_6F_5), 62.0 (*o*-C_5H_7N), 41.8 (*m*-C_5H_7N), 32.33 (CH_3), 16.0 ppm (*p*-C_5H_7N).

Preparation of [*t*-Bu_3PH][$Cl_2B(C_6F_5)_2$] 2a

$ClB(C_6F_5)_2$ (0.076 g, 0.2 mmol) and tri-*tert*-butylphosphine (0.0405 g, 0.2 mmol) were dissolved in 5 mL of toluene giving a yellow solution. The reaction vessel was filled with H_2 (1000 mbar) and the solution was stirred at room temperature for 2 h. Some precipitate had formed during the process. The reaction mixture was concentrated to half of its original volume and hexane was added to induce precipitation. The mixture was filtered, washed with

hexane and dried *in vacuo*. **2a** was collected as a white solid. Yield: 47 %. Anal. Calcd for $C_{24}H_{28}BCl_2F_{10}P$: C, 46.56; H, 4.56. Found: C, 46.48; H, 4.71. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 5.12 (d, 1H, $^1J_{H\text{-}P}$ = 440 Hz, P-*H*), 1.70 ppm (d, 27H, $^3J_{H\text{-}P}$ = 16 Hz P{(C(CH_3)}$_3$). ^{11}B{^{1}H} NMR ($CDCl_3$, 64 MHz, 293 K): δ -4.5 ppm (br). ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz, 293 K): δ 51.8 ppm (s). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ -134.1 (dd, 4F, $^3J_{FF}$ = 23 Hz, $^4J_{F\text{-}Cl}$ = 7 Hz, *o*-C_6F_5), -161.6 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -166.8 ppm (td, 4F, $^3J_{FF}$ = 23 Hz, $^5J_{F\text{-}Cl}$ = 7 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 293 K): δ 147.3 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *o*-C_6F_5), 139.2 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *p*-C_6F_5), 136.9 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *m*-C_6F_5), 37.4 (d, $^1J_{C\text{-}P}$ = 28 Hz, P{*C*(CH_3)}$_3$), 30.0 ppm (s, P(C(*C*H_3)$_3$). X-ray quality crystals were obtained from a mixture of toluene/hexane at 25 °C.

X-ray Crystal Structure Analysis of **2a**: formular $C_{24}H_{28}BCl_2F_{10}P$, *M*r = 619.14, Monoclinic, $P2_1/m$, *a* = 8.8527(1), *b* = 15.7511(2), *c* = 19.8253(3) Å, β = 95.993(2)°, *V* = 2749.33(6) Å^3, *Z* = 4, D_c = 1.496 g cm^{-1}, μ = 0.376 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 27971 reflections collected, 6555 independent [$R_{(int)}$ = 0.0455] and 4858 observed reflections [$I > 2\sigma(I)$], 356 refined parameters, *R* = 0.0352, *w*R$_2$ = 0.0830. CCDC 736258.

Preparation of *t*-Bu_3P-$BH(C_6F_5)_2$ 2b

In a NMR tube a suspension of $HB(C_6F_5)_2$ (0.0346 g, 0.1 mmol) in toluene-d_8 (0.5 mL) was prepared. Tri-*tert*-butylphosphine (0.02 g, 0.1 mmol) was then added to the suspension. The tube was capped with a rubber septum, and the suspension was vigorously shaken until all solid had dissolved (approximately 5 min). Anal. Calcd for $C_{24}H_{28}BF_{10}P$: C, 52.58; H, 5.15. Found: C, 52.50; H, 5.14. ^{1}H NMR (toluene-d_8, 200 MHz, 293 K): δ 4.20 (br, 1H, B-H), 1.11 ppm (d, 27H, $^3J_{H\text{-}P}$ = 12 Hz, P{(C(CH_3)}). ^{11}B{^{1}H} NMR (toluene-d_8, 64 MHz, 293 K): δ -27.4 ppm (br). ^{31}P{^{1}H} NMR (toluene-d_8, 81 MHz, 293 K): δ 47.6 ppm (br). ^{19}F NMR (toluene-d_8, 188 MHz, 293 K): δ -124.56 (br, 4F, *o*-C_6F_5), -158.87 (t, 2F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -164.18 ppm (br, 4F, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 50 MHz, 293 K): δ 148.5 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *o*-C_6F_5), 140.3 (dm, $^1J_{C\text{-}F}$ = 223 Hz, *p*- C_6F_5), 138.0 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *m*-C_6F_5), 39.6 (d, $^1J_{C\text{-}P}$ = 18 Hz, P{*C*(CH_3)}$_3$), 31.1 ppm (s, P(C(*C*H_3)$_3$).

Preparation of [*t*-Bu_3PH][$H_2B(C_6F_5)_2$] 2c

$HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and tri-*tert*-butylphosphine (0.0405 g, 0.2 mmol) were dissolved in 5 mL of toluene giving a slurry. The reaction vessel was filled with H_2 (1000 mbar) and the solution was stirred at 80 °C for 24 h. The reaction mixture was then concentrated to half of its original volume and hexane was added to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as a white solid. Yield: 78 %. Anal. Calcd for $C_{24}H_{30}BF_{10}P$: C, 52.39; H, 5.50. Found: C, 52.27; H, 5.41. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 5.12 (d, 1H, $^1J_{H\text{-}P}$ = 450 Hz, P-*H*), 3.01 (q, br, 1H, $^1J_{H\text{-}B}$ = 90 Hz, B-H), 1.70 ppm (d, 27H, $^3J_{H\text{-}P}$ = 16 Hz P{(C(CH_3)}$_3$). ^{11}B{^{1}H} NMR ($CDCl_3$, 64 MHz, 293 K): δ -30.2 ppm (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz, 293 K): δ 53.9 ppm (s). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ -134.1 (d, 4F, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), -165.9 (t, 2F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -168.0 ppm (t, 4F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 293 K): δ 147.5 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *o*-C_6F_5), 139.7 (dm, $^1J_{C\text{-}F}$ = 244 Hz, *p*-C_6F_5), 136.4 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *m*-C_6F_5), 36.9 (d, $^1J_{C\text{-}P}$ = 28 Hz, P{*C*(CH_3)}$_3$), 30.2 ppm (s, P(C(*C*H_3)$_3$).

Preparation of $[Mes_3PH][Cl_2B(C_6F_5)_2]$ 3a

$ClB(C_6F_5)_2$ (0.0380g, 0.1mmol) and trimesityl phosphine (0.0388 g, 0.1 mmol) were dissolved in 2 mL of toluene giving a pink solution. The reaction vessel was filled with H_2 (1000 mbar) and the solution was stirred at room temperature for 2 h. The reaction mixture was then concentrated to half of its original volume and hexane was added to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. **3a** was collected as a white solid. Yield: 30 %. Anal. Calcd for $C_{39}H_{34}BCl_2F_{10}P$: C, 58.16; H, 4.26. Found: C, 58.08; H, 4.20. ^{1}H NMR (toluene-d_8, 200 MHz, 293 K): δ 8.48 (d, 1H, $^1J_{H\text{-}P}$ = 472 Hz, P-H), 6.52 (s, 6H, P(C_6H_2)$_3$), 2.16 (s, 9H, P(C_6H_2Me-*4*)), 1.95 (s, 9H, P(C_6H_2Me-*2*)), 1.65 ppm (s, 9H, P(C_6H_2Me-*6*)). ^{11}B{^{1}H} NMR (toluene-d_8, 64 MHz, 293 K): δ -4.7 ppm (br). ^{31}P{^{1}H} NMR (toluene-d_8, 81 MHz, 293 K): δ -25.7 ppm (s). ^{19}F NMR (toluene-d_8, 188 MHz, 293 K): δ -132.5 (d, 4F, $^3J_{F\text{-}F}$ = 24 Hz, *o*-C_6F_5), -162.5 (t, 2F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -167.1 ppm (t, 4F, $^3J_{F\text{-}F}$ = 21 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 50 MHz, 293 K): δ 148.3 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *o*-C_6F_5), 146.4 (*para*-C_6H_2), 143.9 (*ortho*-C_6H_2), 140.0 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *p*-C_6F_5), 137.2 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *m*-C_6F_5), 132.5 (*meta*-C_6H_2), 112.3 (d, $^1J_{C\text{-}P}$ = 81 Hz,

P-C_6H_2), 21.8 (C_6H_2Me-6), 21.6 (C_6H_2Me-4), 19.3 ppm (C_6H_2Me-2). X-ray quality crystals were obtained from toluene/hexane solution at 25 °C.

X-ray Crystal Structure Analysis of **3a**: formular $C_{39}H_{34}BCl_2F_{10}P$, *M*r = 805.34, Monoclinic, $P2_1/c$, a = 8.2098(1), b = 19.2927(2), c = 23.8105(2) Å, β = 95.018(1)°, V = 3756.87(7) Å^3, Z = 4, D_c = 1.424 g cm^{-1}, μ = 0.294 mm^{-1}, λ = 0.71073 Å, T = 183(2) K, 79873 reflections collected, 11466 independent [$R_{(int)}$ = 0.0331] and 8553 observed reflections [$I > 2\sigma(I)$], 491 refined parameters, R = 0.0455, wR_2 = 0.1165. CCDC 736259.

Preparation of [Mes_3PH][$HB(C_6F_5)_3$] 3b

$HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and trimesityl phosphine (0.0776 g, 0.2 mmol) dissolved in 5 mL of toluene giving a slurry solution. The reaction vessel was filled with H_2 (1000 mbar) and the reaction mixture was stirred at room temperature for 8 h. The reaction mixture was concentrated to half of its original volume and hexane was added to induce precipitation. The mixture was filtered, washed with hexane and dried in vacuo. The product was collected as a white solid. Yield: 56 %. Anal. Calcd for $C_{45}H_{35}BF_{15}P$: C, 59.89; H, 3.91. Found: C, 59.67; H, 3.61. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 8.06 (d, 1H, $^1J_{H\text{-}P}$ = 456 Hz, P-H), 7.12 (d, 6H, $^4J_{H\text{-}P}$ = 12 Hz, P(C_6H_2)$_3$), 2.37 (s, 9H, P(C_6H_2Me-4), 2.27 (s, 9H, P(C_6H_2Me-2)), 1.99 ppm (s, 9H, P(C_6H_2Me-6)). ^{11}B{^{1}H} NMR ($CDCl_3$, 64 MHz, 293 K): δ -25.6 ppm (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 81 MHz, 293 K): δ -27.0 ppm (s). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ -134.6 (d, 6F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -165.7 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -168.5 ppm (t, 6F, $^3J_{FF}$ = 24 Hz, *m*-C_6F_5).

Preparation of [$H_2B(C_6F_5)$]$_2$ 3c

There was no evidence for signals of the bridging or terminal hydrides in the ^{1}H NMR spectrum. ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): *syn*-[$H_2B(C_6F_5)$]$_2$ δ -136.8 (d, $^3J_{F\text{-}F}$ = 20 Hz, *o*-C_6F_5), -162.1 (t, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -166.6 ppm (t, $^3J_{F\text{-}F}$ = 20 Hz, *m*-C_6F_5). *anti*-[$H_2B(C_6F_5)$]$_2$ δ -137.5 (d, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -160.7 (t, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -166.2 ppm (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{11}B NMR (toluene-d_8, 96 MHz, 293 K): δ 9.5 ppm (br).

Preparation of [TTBPH][$HB(C_6F_5)_3$] 4a

$HB(C_6F_5)_2$ (0.0692 g, 0.2 mmol) and 2,4,6-tri-*tert*-butylpyridine (0.05 g, 0.2 mmol) were dissolved in 5 mL of toluene giving a slurry. The reaction vessel was filled with H_2 (1000 mbar). The solution was stirred at 120 °C for 24 h during which time a white precipitate formed. The reaction mixture was concentrated to half of its original volume and hexane was added to induce complete precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as a white solid. Yield: 38 %. Anal. Calcd for $C_{35}H_{31}BF_{15}N$: C, 55.21; H, 4.10; N, 1.84. Found: C, 55.60; H, 4.18; N, 1.87. ^{1}H NMR ($CDCl_3$, 200 MHz, 293 K): δ 10.66 (br, 1H, N-*H*), 7.72 (s, 2H, Ar-*H*), 3.40 (q, br, 1H, $^1J_{H\text{-}B}$ = 86 Hz, B-*H*), 1.49 (s, 18H, *t*-Bu), 1.40 ppm (s, 9H, *t*-Bu). ^{19}F NMR ($CDCl_3$, 188 MHz, 293 K): δ -134.7 (d, 6F, $^3J_{F\text{-}F}$ = 21 Hz, *o*-C_6F_5), -165.4 (t, 3F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -168.4 ppm (t, 6F, $^3J_{F\text{-}F}$ = 21 Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR ($CDCl_3$, 64 MHz, 293 K): δ -30.7 ppm (s). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz, 293 K): δ 163.7 (*o*-C_5H_2N), 151.0 (*p*-C_5H_2N), 147.8 (dm, $^1J_{C\text{-}F}$ = 238 Hz, *o*-C_6F_5), 139.3 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *p*-C_6F_5), 136.0 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *m*-C_6F_5), 120.7 (*m*-C_5H_2N), 37.9 (*o*-*C*(CH_3)), 37.7 (*p*-*C*(CH_3)), 30.2 (*p*-C(*C*H_3)), 29.0 (*o*-C(*C*H_3)). X-ray quality crystals were obtained from a toluene/hexane solution at 25 °C.

X-ray Crystal Structure Analysis of **4a**: formular $C_{38}H_{38}BF_{15}N$, *M*r = 804.50, Triclinic, *P*$\bar{1}$, *a* = 9.8216(3), *b* = 10.7921(3), *c* = 18.7474(6) Å, α = 74.768(3), β = 77.215(3), γ = 78.314(3)°, *V* = 1847.65(10) Å^3, *Z* = 2, D_c = 1.446 g cm^{-1}, μ = 0.136 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 19560 reflections collected, 6995 independent [$R_{(int)}$ = 0.0421] and 3529 observed reflections [$I > 2\sigma(I)$], 514 refined parameters, *R* = 0.0495, *w*R$_2$ = 0.1148. CCDC 736260.

Preparation of $[H_2B(C_6F_5)]_2$ 3c

^{19}F NMR (toluene-d$_8$, 282 MHz, 293 K): *syn*-$[H_2B(C_6F_5)]_2$ δ -137.1 (*o*-C_6F_5), -161.9 (*p*-C_6F_5), -166.7 ppm (*m*-C_6F_5). *anti*-$[H_2B(C_6F_5)]_2$ δ -137.7 (*o*-C_6F_5), -161.1 (*p*-C_6F_5), -166.3 ppm (t, $^3J_{F\text{-}F}$ = 20 Hz, *m*-C_6F_5). ^{11}B NMR (toluene-d$_8$, 96 MHz, 293 K): δ 8.2 ppm (br).

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[24] pKa values, tBu$_3$P: 11.4; Ph$_3$P: 2.73; (o-MeC$_6$H$_4$)$_3$P: 3.08; (p-MeC$_6$H$_4$)$_3$P: 3.84; **TMP**: 11.07; **TTBP**: 4.02. (a) C. A. Streuli, *Anal.Chem*., 1960, **32**, 985; (b) R. C. Bush, R. J. Angelici, *Inorg. Chem*., 1988, **27**, 681; (c) E. P. Cappellani, S. D. Drouin, G. Jia, P. A. Maltby, R. H. Morris, C. T. Schweitzer, *J. Am. Chem. Soc*., 1994, **116**, 3375; (d) J. Graton, M. Berthelot, C. Laurence, *J. Chem. Soc., Perkin Trans.,* 2001, 2130; (e) H. K. Hall, *J. Am. Chem. Soc*., 1957, **79**, 5444; (f) E. Deutsch, N. K. V. Cheung, *J. Org. Chem*., 1973, **38**, 1123.

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Reversible, Metal-Free Hydrogen Activation by Frustrated Lewis Pairs

Abstract

The Lewis acid cyclohexylbis(pentafluorophenyl)boron **1**, which exhibits about 15% lower Lewis acidity in comparison with $B(C_6F_5)_3$, activates H_2 in the presence of the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), 1,2,2,6,6-pentamethylpiperidine (**PMP**), tri-*tert*-butylphosphine (*t*-Bu_3P) leading in facile reactions at room temperature to heterolytic splitting of dihydrogen and formation of the salts [**TMP**H][$CyBH(C_6F_5)_2$] **2**, [**PMP**H][$CyBH(C_6F_5)_2$] **3** and [*t*-Bu_3PH][$CyBH(C_6F_5)_2$] **4**, which could be dehydrogenated at higher temperatures. The related Lewis acid 1-phenyl-2-[bis(pentafluorophenyl)boryl] ethane **5** exhibiting about 10 % lower Lewis acidity than $B(C_6F_5)_3$ is also capable of splitting H_2 in a heterolytic fashion in the presence of **TMP**, **PMP** and *t*-Bu_3P yielding [**TMP**H][$PhC_2H_4BH(C_6F_5)_2$] **6**, [**PMP**H][$PhC_2H_4BH(C_6F_5)_2$] **7** and [*t*-Bu_3PH] [$PhC_2H_4BH(C_6F_5)_2$] **8**. Under comparable conditions as for **2** – 4, the dehydrogenations of **6** - **8** were much slower. **4b** and **6** were characterized by single crystal X-ray diffraction studies.

Introduction

Dehydrogenation and hydrogenation processes are potential “fuelling” and “refuelling” reactions of a chemical storage system.[1,2] These reactions could occur as 1,2-eliminations/additions from/to a(n) saturated/unsaturated substrate or as binuclear activation processes. Both reactions should be reversible and facile, i.e. possessing low kinetic barriers. This is usually the case when the involved H atoms bear opposite polarizations.[3] Among the compounds with lighter main group elements, which were considered suitable for the given purpose, ammonia borane became a major reseach focus.[4-9] In recent years

respective studies emphasized the dehydrogenation occuring as a 1,2-elimination process. As yet the system is irreversible partly due to thermodynamics, but also due to kinetic short-comings mainly caused by too strong bonds involved. Apparently compounds with heavier main group elements involving generally weaker E-H bonds allow dehydrogenation/hydrogenation reactions with lower barriers. Early model studies on homopolar hydrogenations were carried out in vapor phase with the heavier group 13 elements by trapping intermediates in frozen matrices.[10-12] Similarly, Power and co-workers reported that the highly unsaturated model compound "digermyne" can directly react with H_2 affording a mixture of digermene, digermane and germane.[13] One might speculate that the process takes the course of a direct 1,2-addition processes with simultaneous addition and splitting of the H_2 molecule or with bicentered radical type additions.[3] The mentioned reversible heteropolar binuclear activation pathway of H_2 as introduced by the work of Stephan and his co-workers established a new so-called "metal-free" way of hydrogenation/dehydrogenation. Frustrated Lewis pairs (FLPs), which are main group element "unquenched" Lewis acid-base pairs. The constituents stay remote by steric hindrance forming encounter complexes.[14-16] For instance, the addition of H_2 to the intramolecular Lewis pair $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ resulted in a zwitterionic phosphonium borate salt $(C_6H_2Me_3)_2PH^+(C_6F_4)B^-H(C_6F_5)_2$, thus activating H_2 in a heteropolar fashion at two reaction centers.[17] Due to their high molecular weights, such FLP compounds are certainly not suited for H_2 storage. But the given low energy pathways for H_2 activation may show new directions to develop efficient storage materials. In particular we thought it necessary to acquire more insights into the conditions for reversibility of the underlying chemical processes.

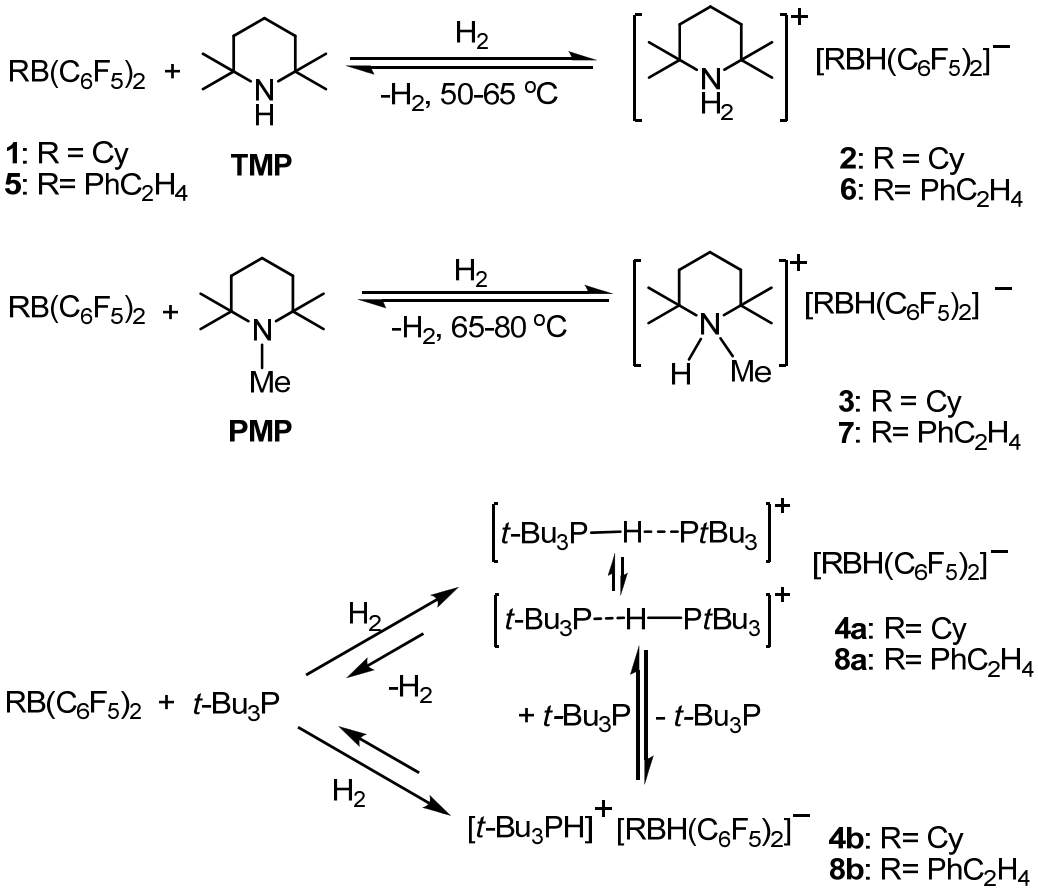
Following the pioneering work of Stephan, an increasing number of FLPs were studied exploring the chemical influence of the Lewis base.[18-38] It was found that the Lewis base function is not limited to phosphine centers, but could be extended to sterically demanding amines, imines, or N-heterocycylic carbenes. In contrast, the influence of the Lewis acid was studied much less. In the majority of FLPs $B(C_6F_5)_3$ was used. To extend the series of functional Lewis acids, our group has explored the role of

1,8-bis(dipentafluorophenyl)naphthalene, $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ in the activation of H_2 with bulky Lewis bases.[39,40] The hydrogenation process was found to proceed in a facile manner, but reversibility of the conversions could not be achieved. Tuning the Lewis acidity it was found that $B(p\text{-}C_6F_4H)_3$ with about 5 % less acidity compared to $B(C_6F_5)_3$ (Gutmann-Beckett's method[41-44]) and presumably due to the changed electronics the FLP with $(o\text{-}C_6H_4Me)_3P$ enabled reversible activation of H_2 at room temperature.[28] Since in this case the change in the sterics and electronics of the Lewis acid was not much, we thought that related variations of the $B(C_6F_5)_3$ master compound might not only lead to reversibly activating systems, but also to a conceptual conclusion of how to steer FLPs toward revesibility.

Results and Discussion

With regard to reversible of H_2 release, we aimed at the exploration of the Lewis acids cyclohexylbis(pentafluorophenyl)boron **1** ($CyB(C_6F_5)_2$) and 1-phenyl-2-[bis (pentafluorophenyl)boryl]ethane **5** ($PhC_2H_4B(C_6F_5)_2$) as FLP components modified for reduced Lewis acidity with respect to $B(C_6F_5)_3$. According to the Gutmann-Beckett's method[41-44] these Lewis acids showed reduced acidities by about 15% and 10%. They were tested for reversible H_2 up-take in the presence of various bulky N,P-Lewis bases as shown in Scheme 4.1.

To prepare $CyB(C_6F_5)_2$ (**1**), $HB(C_6F_5)_2$ was treated in a hydroboration reaction with 1 equiv. of cyclohexene in toluene, which afforded **1** as a white solid in 92 % yield. The ^1H NMR spectrum showed signals for the cyclohexyl group at 2.04 (m, 1H, CH), 1.67 (m, 4H, CH_2), 1.20 ppm (m, 6H, CH_2). The ^{19}F NMR spectrum [δ -132.0 (*o*-), -149.9 (*p*-), -162.2 (*m*-C_6F_5) (C_6D_6)] was consistent with the presence of a three- coordinate boron atom ($\Delta\delta_{m,p}$ = 12.3). We reckoned that the steric congestion of **1** would still be close to that of $B(C_6F_5)_3$ and any difference in the FLP reactivity of **1** was expected to originate from an electronic effect, i.e. its lower Lewis acidity, which was thought to be translated into a considerably weaker *B-H* bond of the tetracoordinate borate species with concomitant higher propensity for dehydrogenation.



Scheme 4.1

Exposure of a toluene solution of the stoichiometric mixture of **1** and 2,2,6,6-tetramethylpiperidine (**TMP**) to an atmosphere of H_2 (1000 mbar) for 30 min afforded the H_2 cleaved ionic product [**TMP**H][HBCy(C_6F_5)$_2$] **2** (Scheme 4.1), which was isolated as a white solid in 76 % yield. In the ^{1}H NMR spectrum **2** displayed a broad B*H* resonance at 2.67 ppm and a N*H* resonance at 4.74 ppm. The ^{19}F NMR spectrum featured a set of typical C_6F_5-borate resonances at δ -132.7 (*o*-), -164.6 (*p*-) and -167.1 (*m*-C_6F_5) ppm. The ^{11}B NMR signal was found to be split into a doublet at -15.5 ppm with a $^1J_{HB}$ coupling of 88 Hz supporting the presence of a boron bound H atom. Interestingly, **2** was quite unstable in solution indeed gradually releasing H_2 at room tempeature. The H_2 liberation became accelerated when the solution was heated to 50 °C. The dehydrogenation reaction of **2** proceeded then so quickly that within 30 min the yield of free CyB(C_6F_5)$_2$ and **TMP** amounted to more than 80 % (Figure 4.1, curve 1). This is

indeed one of the rare examples of a B,N FLP reversibly activating H_2 in solution, but apparently also in the solid state at room temperature, where **2** showed also slow release of H_2.

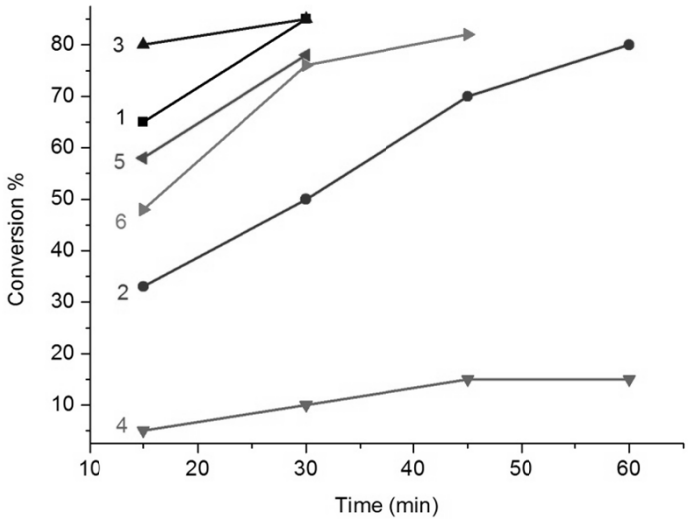


*Figure 4.1 Dehydrogenation of **2**, **3**, **6** and **7** in C_6D_6 at various temperatures. Curve 1: **2** at 50 °C, curve 2: **3** at 65 °C, curve 3: **3** at 80 °C, curve 4: **6** at 50 °C, curve 5: **6** at 65 °C, curce 6: **7** at 80 °C.*

Modifying also the base component we then studied the H_2 reaction of the FLP **PMP**···$BCy(C_6F_5)_2$ (**PMP** = 1,2,2,6,6-pentamethyl piperidine) according to Scheme 4.1 by exposure of a toluene solution of the stoichiometric mixture of **PMP** and $BCy(C_6F_5)_2$ to an atmosphere of H_2 (1000 mbar) for 1 h at room temperature. The reaction observed resulted in the formation of the ionic product [**PMP**H][$HBCy(C_6F_5)_2$] **3** isolated as an analytically pure, white solid in 72 % yield (Scheme 4.1). In the ^{1}H NMR spectrum **3** featured broad N*H* and *BH* resonances at 5.42 and 2.70 ppm and in the ^{11}B NMR spectrum a signal at -15.7 ppm with a $^1J_{BH}$ coupling of 80 Hz. The reaction with H_2 turned out to be reversible, as well, occuring, however, at the somewhat elevated temperature of about 65 °C. The maximum conversion rate in a closed system was found to be about 80 % within 1 h (Figure 4.1. curve 2). At 80 °C, the maximum conversion was 85 % within 30 mins (Fingure 4.1, curve 3).

When the FLP *t*-$Bu_3P\cdots Cy(C_6F_5)_2$ containing a phosphorus Lewis base, was reacted with H_2 at room temperature, a white product was isolated in 74 % yield after work-up. The NMR pursuit of the reaction mixture revealed in the ^{11}B NMR spectrum a broad signal located at -22.2 ppm. Surprisingly, in the ^{1}H NMR spectrum (C_6D_6) two P*H* resonances appeared at 4.61 (**4a**) and 5.71 ppm (**4b**) with $^{1}J_{HP}$ couplings of 438 and 453 Hz and in the ^{31}P NMR spectrum the corresponding resonances were found at 56.4 and 52.2 ppm (Figure 4.2). The MAS ^{31}P NMR of solid **4** also exhibited two signals at 66.7 (broad) and 59.2 (sharp) ppm. Especially based on the relatively large chemical shift difference these could be attributed to the presence of a crystal mixture of **4a** and **4b**.

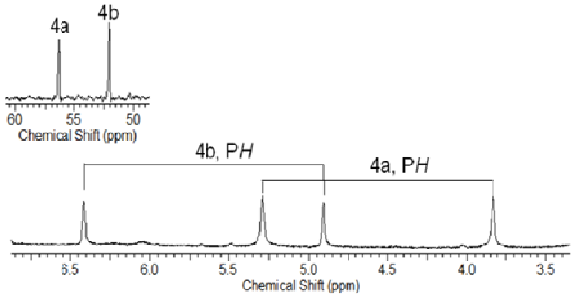


Figure 4.2 $^{31}P\{^{1}H\}$ *NMR (insert) and* ^{1}H *NMR spectrum of* ***4*** *in* C_6D_6 *at r.t.*

It is interesting to note that when the FLP *t*-$Bu_3P\cdots CyB(C_6F_5)_2$ was reacted with D_2, the ^{1}H NMR spectrum also gave two P*H* resonances at 5.52 and 4.44 ppm, and the ^{31}P NMR spectrum exhibited four resonances at 56.8 (s, *P*H), 55.8 (t, *P*D), 52.9 (s, *P*H), 52.0 (t, *P*D) (Figure 4.3). This observation suggested an exchange reaction between D and H. One assumption was that the reaction was initiated by the release of *tert*-butyl cation from the generated [*t*-$Bu_3PD]^+$ cation. The relatively stable carbocation $[(CH_3)_3C]^+$ became then deprotonated by another molecule of *t*-Bu_3P to generate isobutylene $CH_2{=}C(CH_3)_2$, which then inserted into the intermediate [*t*-Bu_2PD] compound to generate a D-labelled *t*-Bu_3P. The release of isotubene and *t*-Bu_2PH from the cation [*t*-$Bu_3PH]^+$ has also been put forward for the [*t*-Bu_3PH][$HB(p\text{-}C_6F_4H)_3$] case published by Stephan's group.[45] Also in this case evidence for the appearance of free $CH_2{=}C(CH_3)_2$ could not be provided, even in presence of a great

excess of *t*-Bu_3P. We assumed the isobutylene insertion reaction was approximately as fast as the isobutylene generation, a circumstance, which naturally is expected to prevent detection of the free olefin. Once the isobutylene generated, it quickly inserts (Scheme 4.2).

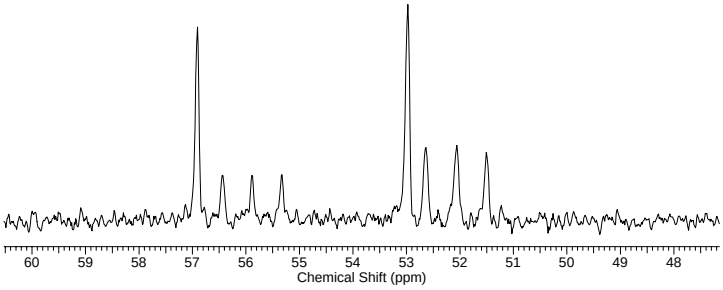
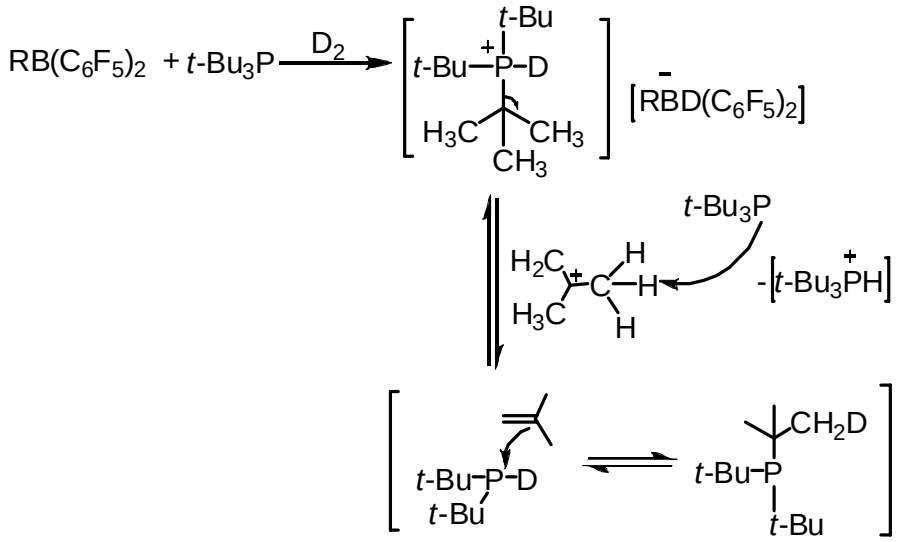


Figure 4.3 $^{31}P\{^{1}H\}$ *NMR spectrum of the FLP t-*$Bu_3P\cdots CyB(C_6F_5)_2$ *to react with* D_2 *in* C_6D_6 *at r.t.*



Scheme 4.2

The products of the reactions of the FLP *t*-$Bu_3P\cdots CyB(C_6F_5)_2$ with H_2 or D_2 in benzene were two species coexisting in solution and in solid state. One product should be the expected ionic product [*t*-Bu_3PH][$CyBH(C_6F_5)_3$] **4b**, which is consistent with the NMR spectra (^{1}H NMR: 5.71 ppm; ^{31}P NMR: 52.2 ppm) and the X-ray diffraction analysis, in which the anion and the cation are oriented "face-to-face" to each other with a non-bonding H1···H2 distance of 2.63 Å (Figure 4.4). For the other species, several assumptions are given. One assumption

was the coulombic ion pair of **4a**, in which the cation and the anion were anticipated to be held together additionally by multiple, but generally weak, CH···F, PH···F or BH···HP dihydrogen bonding interactions. These weak interactions of the hydrogen or dihydrogen bonding type were not detectable by NMR spectroscopy. T_1(min) or NOE measurements did not provide any hint for correlation effects between the cation and the anion. Another proposal for the structure of **4a** was the formation of [*t*-Bu_2PH_2][CyBH(C_6F_5)$_3$] (or [*t*-Bu_2PHD][CyBH(C_6F_5)$_3$]), based on the generation of *t*-Bu_2PH during the H-D (H) exchange reaction. But no *J*(HD) *J*(PD) coupled resonances were observed in the ^{1}H NMR or the ^{31}P NMR spectrum and a ^{31}P NMR resonance was also not detected expected for the phosphonium cation [*t*-Bu_2PH_2]$^+$ at 26 ppm.[45] So this proposal could not be verified by appropriate spectroscopic compliance, as well.

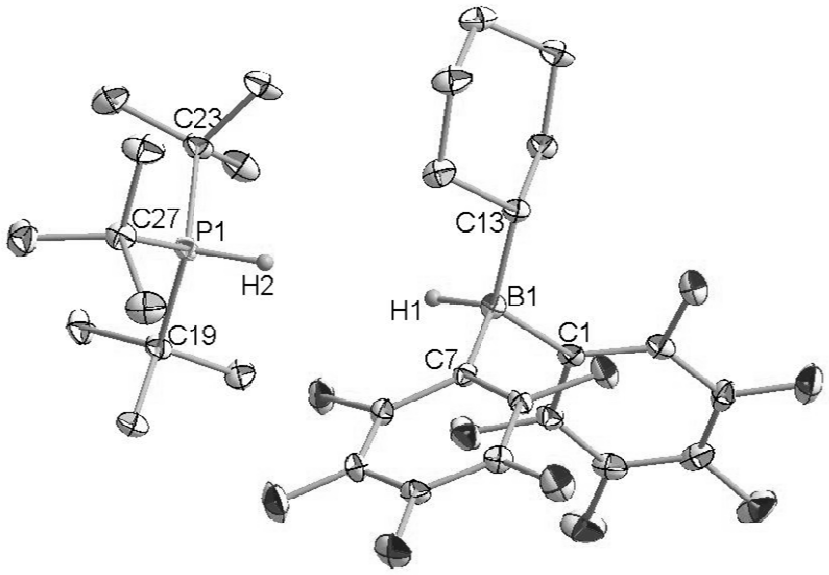


Figure 4.4 Molecular structure of the ion pair **4b**. *Hydrogen atoms except for the PH and BH are omited for clarity.*

Based on the fact that the isolated product mixture dissolved in the unpolar solvent C_6D_6 giving two different species, but in the polar solvent $CDCl_3$ only one species, we first of all reckoned that both compounds are structurally related. We suspected the unusual hydrogen bonded species [*t*-Bu_3P-H···P*t*Bu_3][CyBH(C_6F_5)$_2$] to be **4a** (Scheme 4.1). In order to prove

this assumption, we then varied the ratios of *t*-Bu_3P to $CyB(C_6F_5)_2$ in the reaction with H_2 and monitored the reaction course. The ratio of the products **4a** or **4b** turned out to be sensetive with respect to the applied amount of *t*-Bu_3P. For instance in the cases of the 1:2 or 1:1 ratios with respect to $CyB(C_6F_5)_2$, the majority of the product is **4b** [*t*-Bu_3PH][$CyBH(C_6F_5)_3$] and **4a** is formed in small amounts only. But when the *t*-Bu_3P to $CyB(C_6F_5)_2$ ratio was increased to 2:1, **4a** became the predominant product and **4b** could not be detected at all when *t*-Bu_3P was present in great excess (*t*-Bu_3P: $CyB(C_6F_5)_2$ = 5:1). This observation suggested that **4a** is formed from **4b** in an equilibrium reaction via the addition of *t*-Bu_3P (Scheme 4.1). **4a** featured a P*H* resonance at 4.61 ppm in ^1H NMR spectrum with a $^1J_{HP}$ coupling of 438 Hz. The lower *J*(HP) coupling of the P*H* signal of **4a** compared to **4b** of 453 Hz could indeed be related to [P-H···P] hydrogen bonding, since the hydrogen bonding of P(*t*Bu)$_3$ is expected to withdraw electron densities from the P-H bond and decrease its bond order. Additional experiments showed that both **4a** and **4b** were not stable in solution and gradually underwent dehydrogenation reactions. According to ^1H NMR and ^{31}P NMR pursuits, the P*H* signals of **4a** disappeared first at room temperatue accompanied by the appearance of signals for free H_2 located at 4.45 ppm and of free *t*-Bu_3P. **4b** seemed somewhat more stable in this process, but

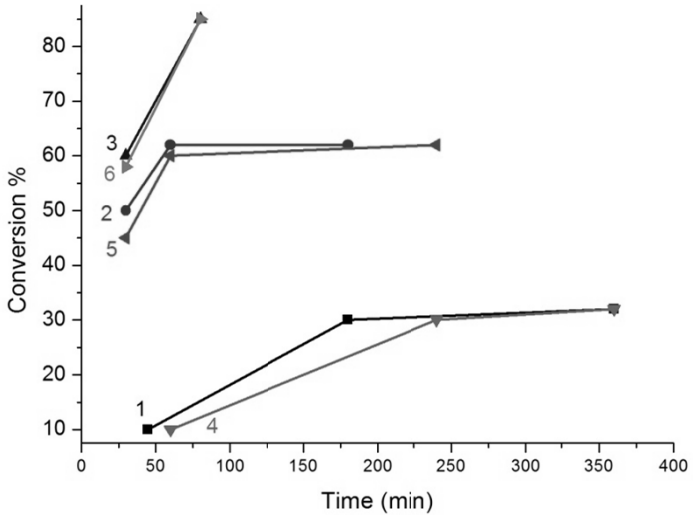


*Figure 4.5 Dehydrogenations of **4** and **8** in C_6D_6 at various temperatures pursued by ^1H NMR. Curve 1: **4** at r.t., curve 2: **4** at 50 ^oC, curve 3: **4** at 80 ^oC, curve 4: **8** at r.t., curve 5: **8** at 50 ^oC, curve 6: **8** at 80 ^oC.*

it disappeared also at elevated temperatures. Further investigations demonstrated that the dehydrogenation reaction of the mixture of **4** is quite temperature dependent. At room temperature and based on NMR spectroscopy, the conversion was about 30 % within 3 h in C_6D_6 solution (Figure 4.5, curve 1). While at 50 ^oC, the conversion reached 60 % (Figure 4.5, curve 2), and at the higher temperature of 80 ^oC more than 80 % of free *t*-Bu_3P and $CyB(C_6F_5)_3$ were regenerated within 1 h (Figure 4.5, curve 3).

The series of FLP combinations applied up to now, showed that the Lewis acidity of the Lewis acid is a crucial factor to achieve reversibility in the H_2 splitting. In addition it was found earlier that H_2 can be heterolytically cleaved by the *t*-$Bu_3P\cdots B(C_6F_5)_3$, **TMP**$\cdots B(C_6F_5)_3$ or **PMP**$\cdots B(C_6F_5)_3$ FLPs, but none of the corresponding salts [*t*-Bu_3PH][$HB(C_6F_5)_3$], [**TMP**H][$HB(C_6F_5)_3$] and [**PMP**H][$HB(C_6F_5)_3$][46] could release H_2 even at higher temperatures. This inability was prevailingly attributed to a too high B-H bond strength in the $[HB(C_6F_5)_3]^-$ anion related to the higher Lewis acidity of $B(C_6F_5)_3$.

In order to further substantiate the given assumption of the Lewis acidity influence, we selected the Lewis acid $PhCH_2CH_2B(C_6F_5)_2$ **5** with a Lewis acidity between those of $BCy(C_6F_5)_2$ **1** and $B(C_6F_5)_3$. **5** was then applied in FLPs in combination with the same Lewis bases as for **1** (Scheme 4.1). As expected, the FLPs **TMP**$\cdots PhCH_2CH_2B(C_6F_5)_2$ and **PMP**$\cdots PhCH_2CH_2B(C_6F_5)_2$ induced heterolytic splitting of H_2 at room temperature to form white solids of the ionic products [**TMP**H][$PhCH_2CH_2BH(C_6F_5)_2$] **6** and [**PMP**H][$PhCH_2CH_2BH(C_6F_5)_2$] **7** in 85 % and 83 % yield. Both of these ionic compounds featured in the ^1H NMR signals of the N*H* resonances with chemical shifts at 4.52 and 5.49 ppm in C_6D_6 similar to those of **2** and **3** indicating the presence of the same cationic species. In addition, the ^{19}F NMR resonances of **6** (-133.7 (*o*-), -164.3 (*p*-), -166.9 (*m*-C_6F_5) ppm) and **7** (-133.6 (*o*-), -164.1 (*p*-), -167.0 (*m*-C_6F_5) ppm) are comparable to those of **2** and **3**. As anticipated, both compounds **6** and **7** released H_2 under mild conditions, but the rates were not quite as high as in the $BCy(C_6F_5)_2$ cases. After 1 h at 50 ^oC, the conversion of **6** was only 15% (Figure 4.1, curve 4), while for **2** it had reached more than 80 % under the same conditions. In order to accomplish the same yields in the dehydrogenation process as for **2**, **6** required temperatures of about 65 ^oC. Due to the higher Lewis acidity of $PhCH_2CH_2B(C_6F_5)_2$, **5** was

supposed to generate a stronger B-H bond in the hydrido borate anion than $BCy(C_6F_5)_2$ consequently requiring more severe conditions in dehydrogenation batches.

Single-crystals of **6** were grown from a toluene/hexane solution at 243 K and analyzed by X-ray diffraction (Figure 4.6). After refinement of the N*H*$_2$ and B*H* hydrogens a close B-H···H-N bonding contact of 1.88 Å could be extracted, consistent with strong dihydrogen bonding. Similar dihydrogen bonding was observed in the X-ray crystal structure of [*t*-$BuNH_2$-CH_2Ph][$HB(C_6F_5)_3$], in which the distance between one of the N*H*$_2$ protons and the B-*H* hydride was 1.87(3) Å.[47] Despite this close contact, no evidence was found for spontaneous dehydrogenation or dehydrogenations to take place at elevated temperatures. **6**, however, released H_2 at 65 °C quite fast. This again provided evidence that reformation of H_2 from a [LBH][LAH] pair (LB: Lewis base; LA: Lewis acid) is mainly correlated with the strength of the B-H bond rather than with a kinetically feasible short contact between the protonic and hydridic hydrogen atoms.

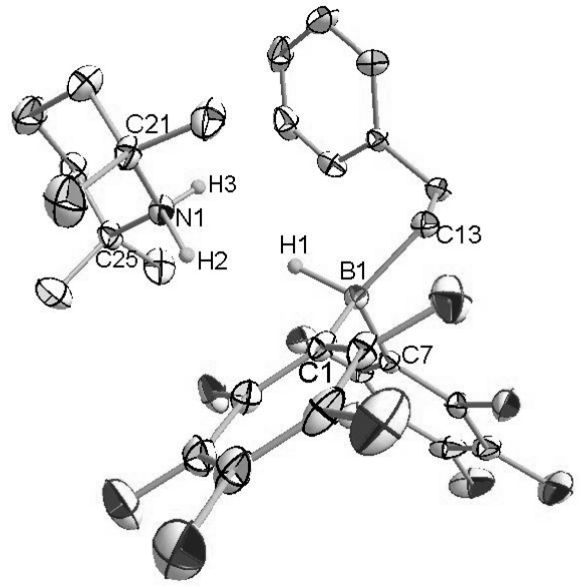


Figure 4.6 Molecular structure of ***6****, 30 % probability thermal ellipsoids are shown. Hydrogen atoms except for the NH and BH are omitted for clarity.*

The FLP *t*-Bu_3P···$BPhCH_2CH_2(C_6F_5)_2$ also enabled heterolytic activation of H_2 in the

same way as the *t*-$Bu_3P\cdots CyB(C_6F_5)_2$ system. The isolated product exhibited again two different P*H* resonances at 5.34 (**8b**, [*t*-Bu_3P-H$\cdots$P*t*Bu_3][$PhCH_2CH_2BH(C_6F_5)_2$]) and at 4.13 ppm (**8a**, [*t*-Bu_3P-H][$PhCH_2CH_2BH(C_6F_5)_2$]) in the ^1H NMR spectrum in C_6D_6 solution with $^1J_{HP}$ coupling constants of 447 and 432 Hz and in the ^{31}P NMR spectrum also two signals were located at 53.5 (**8b**) and 57.4 ppm (**8a**). The solid state ^{31}P NMR also gave two different resonances of 59.3 (sharp, **8b**) and 64.0 (broad, **8a**) ppm indicating that both compounds are co-crystallizing. A similar observation was made as for **4**: when **8** was dissolved in the more polar solvent $CDCl_3$, only one species could be observed which was attributed the structure of the solvated ions of **8b**.

By analogy to **4** we assume that there are two coexisting ion pairs **8a** and **8b** in benzene solution, and in the solid state we suppose in analogy to **4** the presence of a crystalline mixture of **8a** and **8b** (Scheme 4.1). Moreover, the ion pair **8a** seemed to be quite unstable in solution accompanied by fast H_2 loss, while **8b** in $CDCl_3$ was found to be more stable. At the elevated temperature of 80 ^oC, the conversion of the dehydrogenation of the mixture of **8** also increased to more than 80 % (Figure 4.4, curve 6).

Conclusion

In a tuning effort the two Lewis acids $CyB(C_6F_5)_2$ **1** and $PhC_2H_4B(C_6F_5)_2$ **5** were applied as FLPs in combination with the bulky Lewis bases **TMP**, **PMP** and *t*-Bu_3P to split dihydrogen heterolytically. In comparison with the known chemistry of the "parent" Lewis acid $B(C_6F_5)_3$, reversibility of the H_2 uptake was achieved for $CyB(C_6F_5)_2$ and $PhC_2H_4B(C_6F_5)_2$. Based on Gutmann's method, the relative Lewis acidities of the fluorinated boron Lewis acids are as follows: $B(C_6F_5)_3 > B(p\text{-}C_6F_4H)_3 > PhC_2H_4B(C_6F_5)_2 > CyB(C_6F_5)_2$. Changes in the Lewis bases turned out to be of secondary importance for hydrogenation/dehydrogenation reversibility. The main factor for reversible activation of H_2 was found to be the diminished Lewis acidity with regard to $B(C_6F_5)_3$ accomplished in this work by variation of one of the boron substituents.

Experimental part

General consideration: All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze-thaw cycles prior to use. All organic reagents were purchased from Aldrich and used without further purification. $HB(C_6F_5)_2$ was synthesized according to the literature,[48,49] cyclohexene and styrene were dried before use. ^1H NMR, ^{19}F NMR and $^{11}B\{^1H\}$ NMR $^{31}P\{^1H\}$ NMR data were recorded on a Varian Gemini-300 spectrometer. Chemical shift are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F NMR, $^{11}B\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR were referenced to $CFCl_3$, $BF_3{\cdot}OEt_2$ and 85 % H_3PO_4, respectively. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoKα radiation, λ = 0.71073 Å).[50] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, absorption correction and data reduction were performed with the Oxford program suite *CrysAlisPro*.[51] The structures were solved with direct methods (*SHELXS-97*) and were refined by full-matrix least-squares methods on F^2 (*SHELXL-97*).[52] All programs used during the crystal structure determination processes are included in the *WINGX* software.[53] The program *PLATON*[54] was used to check the result of the X-ray analyses.

Synthesis of $CyB(C_6F_5)_2$ 1 and $PhC_2H_4B(C_6F_5)_2$ 5

These two compounds were prepared in a similar fashion and thus only one preparation is detailed. $HB(C_6F_5)_2$ (0.346 g, 1 mmol) and cyclohexene (0.1 g, 1.2 mmol) were disolved in 5 mL of toluene. The slurry solution turned clear after 5 min, allowed the solution stirred for additional 30 min. Then the solvent was removed *in vacuo* to obtain **1** as a

white solid which was washed by hexane and dried *in vacuo*.

$CyB(C_6F_5)_2$ 1. Yield: 92 %. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 2.04 (m, 1H, CH), 1.67 (m, 4H, CH_2), 1.20 ppm (m, 6H, CH_2). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ -132.0 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -149.9 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -162.2 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5).

$PhC_2H_4B(C_6F_5)_2$ 5. Yield: 95 %. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.12 (d, 2H, $^3J_{HH}$ = 6Hz, Ph-*H*), 7.02 (m, 3H, Ph-*H*), 2.70 (t, 2H, $^3J_{HH}$ = 6Hz, CH_2), 2.22 ppm (t, 2H, $^3J_{HH}$ = 6Hz, CH_2). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ -131.6 (d, 4F, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), -148.4 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -162.3 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5).

Lewis acidity tests according to the *Gutmann-Beckett* method in $CDCl_3$.

$^{31}P\{^1H\}$ NMR: Ph_3P=O reference: δ = 29.5. $(Ph_3P{=}O)B(C_6F_5)_3$ reference addcut: δ = 45.5. Reference shift: $\Delta\delta$ = 16.0. $(Ph_3P{=}O)B(Cy)(C_6F_5)_2$ reference addcut: δ = 42.0. Reference shift: $\Delta\delta$ = 12.5. Lewis-acidity relative to $B(C_6F_5)_3$: 78.1 %. $(Ph_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference addcut: δ = 42.3. Reference shift: $\Delta\delta$ = 12.8. Lewis-acidity relative to $B(C_6F_5)_3$: 80.0 %. Et_3P=O reference: δ = 52.8. $(Et_3P{=}O)B(C_6F_5)_3$ reference addcut: δ = 76.3. Reference shift: $\Delta\delta$ = 23.5. $(Et_3P{=}O)B(Cy)(C_6F_5)_2$ reference addcut: δ = 72.8. Reference shift: $\Delta\delta$ = 20.0. Lewis-acidity relative to $B(C_6F_5)_3$: 85.1 %. $(Et_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference addcut: δ = 74.4. Reference shift: $\Delta\delta$ = 21.6. Lewis-acidity relative to $B(C_6F_5)_3$: 91.9 %. ***Gutmann-Beckett* in C_6D_6**. *$^{31}P\{^1H\}$ NMR*: Ph_3P=O reference: δ = 25.3. $(Ph_3P{=}O)B(C_6F_5)_3$ reference addcut: δ = 45.6. Reference shift: $\Delta\delta$ = 20.3. $(Ph_3P{=}O)B(Cy)(C_6F_5)_2$ reference addcut: δ = 42.1. Reference shift: $\Delta\delta$ = 16.8. Lewis-acidity relative to $B(C_6F_5)_3$: 82.8 %. $(Ph_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference addcut: δ = 42.3. Reference shift: $\Delta\delta$ = 17.0. Lewis-acidity relative to $B(C_6F_5)_3$: 83.7 %. Et_3P=O reference: δ = 46.0. $(Et_3P{=}O)B(C_6F_5)_3$ reference addcut: δ = 75.8. Reference shift: $\Delta\delta$ = 29.8. $(Et_3P{=}O)B(Cy)(C_6F_5)_2$ reference addcut: δ = 72.5. Reference shift: $\Delta\delta$ = 26.5. Lewis-acidity relative to $B(C_6F_5)_3$: 88.9 %. $(Et_3P{=}O)B(PhCH_2CH_2)(C_6F_5)_2$ reference addcut: δ = 74.2. Reference shift: $\Delta\delta$ = 28.2. Lewis-acidity relative to $B(C_6F_5)_3$: 94.6 %.

Preparation of [TMPH][CyBH(C_6F_5)$_2$] 2, [PMPH][CyBH(C_6F_5)$_2$] 3, [*t*-Bu_3PH][CyBH(C_6F_5)$_2$] 4, [TMPH][PhC_2H_4BH(C_6F_5)$_2$] 6, [PMPH][PhC_2H_4BH(C_6F_5)$_2$] 7, [*t*-Bu_3PH][PhC_2H_4BH(C_6F_5)$_2$] 8.

2 – **4** and **6** – **8** were all prepared in the same way. Their preparations are described in general form (LA = Lewis acid. LB = Lewis base). Stoichiometric amounts of LA (0.2 mmol) and LB (0.2 mmol) were dissolved in 5 mL of toluene, giving a colorless solution. The reaction vessel was filled with 1000 mbar of H_2 and the solution was stirred at room temperature for 1 h. The reaction mixture was then concentrated to half of its volume, and hexane was added to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*.

Compound 2. CyB(C_6F_5)$_2$ (0.0856 g, 0.2 mmol) and **TMP** (0.0283 g, 0.2 mmol). **2** was obtained as a white solid, yield 76 %. Anal. Calcd for $C_{27}H_{32}BF_{10}N$: C, 56.76; H, 5.65; N, 2.45. Found: C, 56.51; H, 5.60; N, 2.50. ^{1}H NMR (C_6D_6, 300MHz, 298 K): δ 4.74 (br, 2H, N*H*), 2.67 (br, 1H, B*H*), 2.03 (m, 4H, CH_2), 1.70 (m, 4H, CH_2), 1.48(m, 1H, CH), 1.18 (m, 2H, CH_2), 0.72 (overlap, 18H, CH_2, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ -132.7 (d, 4F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -164.6 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -167.1 (t, 4F, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 298 K): δ -15.5 ppm (br).

Compound 3. CyB(C_6F_5)$_2$ (0.0856 g, 0.2 mmol) and PMP (0.034 g, 0.2 mmol). **3** was obtained as a white solid, yield 72 %. Anal. Calcd for $C_{28}H_{34}BF_{10}N$: C, 57.45; H, 5.85; N, 2.39. Found: C, 57.07; H, 5.47; N, 2.04. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 5.42 (br, 1H, N*H*), 2.70 (br, 1H, B*H*), 2.12 (m, 3H, Cy-H), 1.83 (d, 3H, $^3J_{HH}$ = 6 Hz, N-CH_3), 1.45 (m, 2H, Cy-H), 1.26 (m, 6H, Cy-H), 1.04 (m, 2H, CH_2), 0.90 (m, 4H, CH_2), 0.76 (s, 6H, CH_3), 0.34 (s, 6H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -132.5 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -164.9 (t, 2F, $^3J_{FF}$ = 23Hz, *p*-C_6F_5), -167.3 (t, 4F, $^3J_{FF}$ = 23Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -15.7 ppm (br).

Compounds 4a and **4b**. CyB(C_6F_5)$_2$ (0.0856 g, 0.2 mmol) and *t*-Bu_3P (0.04 g, 0.2 mmol). **4a** was obtained as a white solid, yield 74 %. Anal. Calcd for $C_{30}H_{40}BF_{10}P$: C, 56.98; N, 6.38. Found: C, 56.77; H, 6.51. ^{1}H NMR (C_6D_6, 300MHz, 298 K): δ 5.71 (d,

$^1J_{HP}$ = 453 Hz, P*H*, **4b**), 4.61 (d, $^1J_{HP}$ = 438 Hz, P*H*, **4a**), 3.16 (br, 1H, B*H*), 2.23 (m, 1H, CH), 1.97 (m, 4H, CH_2), 1.76 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 0.85 (d, 27H, $^3J_{H-P}$ = 15 Hz P{(C(CH$_3$)}$_3$). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ -132.1 (overlap, *o*-C_6F_5), -165.9 (t, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5, **4b**), -166.8 (t, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5, **4a**), -167.9 (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5, **4b**), -168.4 ppm (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5, **4a**). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz, 298 K): δ 56.4 (**4a**), 52.2 (**4b**) ppm. ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 298 K): δ -22.2 ppm (br).

X-ray Crystal Structure Analysis of **4b**: formula $C_{30}H_{40}BF_{10}P$, *M*r = 632.40, orthorhombic, *Pbca*, *a* = 18.3337(3), *b* = 16.1172(3), *c* = 20.7593(3) Å, *V* = 6134.12(18) Å^3, *Z* = 8, μ = 0.170 mm^{-1}, 43845 reflections collected, 9356 independent (R_{int} = 0.0455), R_1 = 0.0427, wR_2 = 0.0918 (for 5223 observed reflections with $I \geq 2\sigma(I)$ and 396 refined parameters). CCDC 793471.

Compound 6. $PhCH_2CH_2B(C_6F_5)_2$ (0.09 g, 0.2 mmol) and **TMP** (0.0283 g, 0.2 mmol). **6** was obtained as a white solid, yield 85 %. Anal.Calcd. for $C_{29}H_{30}BF_{10}N$: C, 58.70; H, 5.10; N, 2.36. Found: C, 58.42; H, 5.02; N, 2.23. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 7.38 (d, 2H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 7.18 (t, 2H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 7.03 (t, 1H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 4.52 (br, 2H, N*H*), 2.85 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 1.75 (br, 2H, CH_2), 0.89 (m, 2H, CH_2), 0.78 (m, 2H, CH_2), 0.69 (s, 12H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -133.7 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -164.3 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -166.9 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -18.8 ppm (br).

X-ray Crystal Structure Analysis of **6**: formula $C_{29}H_{30}BF_{10}N$, *M*r = 593.35, Triclinic, *P*$\bar{1}$, *a* = 9.4346(2), *b* = 11.4068(3), *c* = 14.4546(3) Å, α = 74.034(2), β = 87.133(2), γ = 68.809(2), *V* = 1392.33(6) Å^3, *Z* = 2, μ = 0.128 mm^{-1}, 28610 reflections collected, 7497 independent (R_{int} = 0.0257), R_1 = 0.0562, wR_2 = 0.1720 (for 5114 observed reflections with $I \geq 2\sigma(I)$ and 385 refined parameters). CCDC 793472.

Compound 7. $PhCH_2CH_2B(C_6F_5)_2$ (0.09 g, 0.2 mmol) and **PMP** (0.034 g, 0.2 mmol). **7** was obtained as a white solid, yield 83 %. Anal.Calcd. for $C_{30}H_{32}BF_{10}N$: C, 59.32; H, 5.31; N, 2.31 . Found: C, 59.53; H, 5.41; N, 2.33. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ

7.42 (d, 2H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 7.26 (t, 2H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 7.13 (t, 1H, $^3J_{HH}$ = 6 Hz, Ph-*H*), 5.49 (br, 1H, N*H*), 2.80 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 1.77 (m, 2H, CH_2), 1.61 (d, 3H, $^3J_{HH}$ = 6 Hz, N-CH_3), 1.23 (t, 2H, $^3J_{HH}$ = 6 Hz, CH_2), 0.79 (m, 4H, CH_2), 0.65 (s, 6H, CH_3), 0.18 ppm (s, 6H, CH_3). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -133.6 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -164.1 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -167.0 (t, 6F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -18.6 ppm (br).

Compounds 8a and **8b**. $PhCH_2CH_2B(C_6F_5)_2$ (0.09 g, 0.2 mmol) and *t*-Bu_3P (0.04 g, 0.2 mmol). **8a** was obtained as a white solid, yield 78 %. Anal.Calcd. for $C_{32}H_{38}BF_{10}P$: C, 58.73; H, 5.85. Found: C,58.59; H,5.72. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.49, 7.25, 7.10 (Ph-*H*), 5.34 (d, $^1J_{HP}$ = 447 Hz, P*H*, **8b**), 4.13 (d, $^1J_{Hp}$ = 432 Hz, P*H*, **8a**), 3.00, 2.81, 1.88, 1.58, 1.22 (CH_2), 0.74 (d, 27H, $^3J_{H\text{-}P}$ = 15 Hz P{(C(CH_3)}$_3$). ^{19}F NMR (C_6D_6, 282 MHz, 298 K): δ -133.1 (overlap, *o*-C_6F_5), -165.6 (t, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5, **8b**), -166.7 (t, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5, **8a**), -167.7 (t, $^3J_{F\text{-}F}$ = 20 Hz, *m*-C_6F_5, **8b**), -168.3 (t, $^3J_{F\text{-}F}$ = 20 Hz, *m*-C_6F_5, **8a**). ^{31}P{^{1}H} NMR (C_6D_6, 121 MHz, 298 K): δ 57.4 (**8a**), 53.5 (**8b**). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 298 K): δ -18.5 ppm (br).

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Heterolytic H_2 Cleavage by Frustrated B/N Lewis Pairs

Abstract

The Lewis acid $B(C_6F_5)_3$ encountered with the Lewis base 2,6-dimethylpiperidine (**DMP**) resulted in the formation of the classical Lewis acid-base adduct **DMP-**$B(C_6F_5)_3$ **1a**, which was anticipated to undergo thermal dissociation to the "unquenched" centers. The free Lewis pair were able to form a Frustrated Lewis Pair (FLP), which induced heterolytic splitting of H_2 affording the ionic product [**DMP**H][$HB(C_6F_5)_3$] **1b**. FLPs, derived from $B(C_6F_5)_3$ and the bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), 1,2,2,6,6-pentamethylpiperidine (**PMP**), could also heterolytically activate H_2 affording the salts [**TMP**H][$HB(C_6F_5)_3$] **2** and [**PMP**H][$HB(C_6F_5)_3$] **3**, respectively. In a VT NMR study the **TMP**/$B(C_6F_5)_3$ reaction was studied in greater detail trying to trace intermediates. The supposed most prominent intermediate, the **TMP**/H_2/$B(C_6F_5)_3$ complex, could however not be detected. The combination of $B(C_6F_5)_3$ with the even more sterically demanding Lewis base 1-ethyl-2,2,6,6,-tetramethylpiperidine (**Et-TMP**) displayed FLP reactivity with H_2, but required the high temperature of 110 ^oC forming [2,2,6,6-$(CH_3)_4C_5H_6NH(CH_2CH_3)$] [$HB(C_6F_5)_3$] **4a**. In the absence of H_2 the combination of $B(C_6F_5)_3$ with **Et-TMP** generated at room temperature a mixture of **4a** and [2,2,6,6-$(CH_3)_4C_5H_6N$=$CHCH_2$-$B(C_6F_5)_3$] **4b**. **4b** was formed via consecutive hydride and proton abstractions with **Et-TMP** as the base generating **4a**. 2,4,6-tri-*tert*-butylpyridine (**TTBP**) exhibiting reduced Lewis basicity as compared to piperidine derivatives showed FLP reactivity with $B(C_6F_5)_3$, which gave in the presence of H_2 the [**TTBP**H][$HB(C_6F_5)_3$] **5** salt as the only product after several hours. The steric demand of the Lewis bases was evaluated by aid of DFT calculations on borane adducts, which roughly correlated with the reaction temperatures of H_2 splitting. **1a**, **1b**, **2**, **3**, **4a, 4b** and **5** were studied by single-crystal X-ray diffraction analyses.

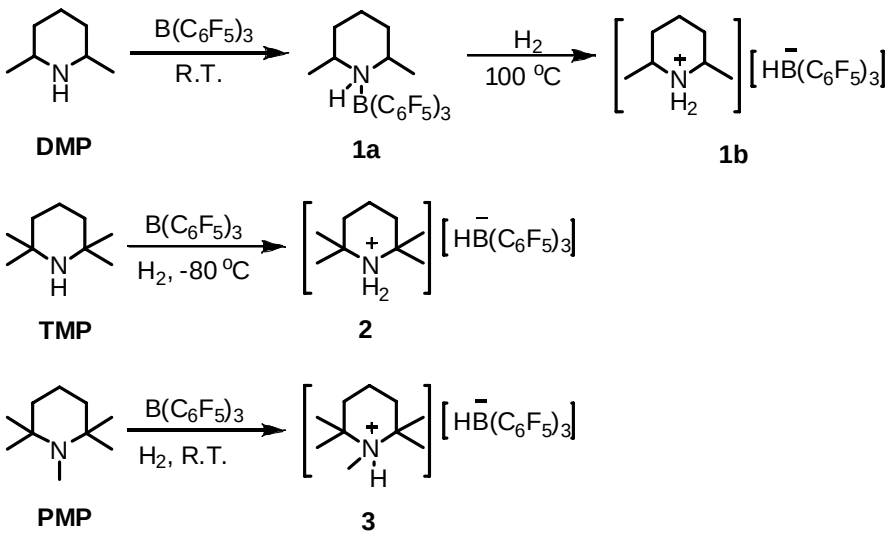
Introduction

The concept of Frustrated Lewis Pairs (FLPs) was put forth by D. W. Stephan et al. after their remarkable discovery that H_2 can reversibly be activated by $[(2,4,6\text{-}C_6H_2Me_3)_2PC_6F_4B(C_6F_5)_2]$,[1] which led to development of the first metal-free catalyst for hydrogenations of bulky imines as one of the fruitful applications of this concept.[2] The steric congestion of Lewis donor and acceptor precludes the formation of classical Lewis adducts, but provokes formation of FLPs with "unquenched" reactivity towards small molecules.[3-5] For instance, the mixture of frustrated phosphines and boranes can activate H_2 heterolytically under very mild conditions,[6] and can undergo 1,2-addition reactions with olefins, as well.[7,8] After the pioneering work of Stephan et al, an increasing number of related FLP systems were found. The frustrated Lewis pairs were extended from the initial boron/phosphine species [9-20] to boron/carbene systems and borane/amine species.[21-24] Some of the resulting ionic products were shown to serve as active catalysts for the hydrogenation of imines, nitriles and aziridines, as well as enamine and silyl enol ethers.[12,24,25] However, the mechanism of the H_2 activation by FLPs is still not fully understood. Theoretical studies proposed that the Lewis donor and acceptor initially form an "encounter complex" with long non-bonding distances between the Lewis centers frequently supported by multiple CH···F interactions. Such relatively weak specific forces, as well as the global electrostatic field of the Lewis pair, caused in sum too small interaction energies to allow proper identification by conventional analytical methodologies. H_2 can insert into this encounter complex being thus activated with heterolytic H-H splitting.[26-27] Recent sophisticated DFT studies by Grimme et al., which included dispersion forces, pointed out that the intermediate formed between H_2 and for instance a P/B FLP could show kinetic stabilization and would thus be spectroscopically detectable under the condition that the P···B non-bonding distance is over 4.5 Å. Otherwise, the H_2 heterolysis would be practically barrierless, once the H_2 molecule had "sneaked" into the FLP complex.[28] Herein, we would therefore like to explore several sterically hindered Lewis bases, mainly piperidine and pyridine derivatives, to modulate the B···N non-bonding distance of the FLP and to study the impact of the varying the B···N

distance on their ability to activate H_2.

Results and Discussion

The reaction of the cyclic *sec*. amine piperidine and $B(C_6F_5)_3$ produced the classical Lewis acid-base adduct $C_5H_{10}N(H)$-$B(C_6F_5)_3$.[29] This adduct turned out to be too stable preventing thermal dissociation and subsequent FLP induced heterolysis of H_2. Consequently the steric bulk of the Lewis base was increased employing 2,6-dimethyl piperidine (**DMP**) in conjunction with $B(C_6F_5)_3$ in toluene. However, still formation of the classical Lewis acid-base adduct **DMP**-$B(C_6F_5)_3$ **1a** was observed (Scheme 5.1). In addition FLP type intermediates could not be traced along the adduct formation process. The ^{19}F NMR spectrum of **1a** was consistent with a Lewis adduct structure revealing however three signals attributed to the *ortho*- (-128.2, -128.5, -138.6 ppm) and *meta*-F (-162.4, -164.4 – -164.6 ppm) and two signals for the *para*-F (-155.2, -157.6 ppm) atom indicating molecular dissymmetry in solution. This was interpreted in terms of hindered rotation of the C_6F_5 rings around the B-C bonds, which apparently arose from steric conflicts between the methyl substituents on the piperidine side and the fluorine atoms on the boron side of the molecule. A singlet resonance in the ^{11}B NMR spectrum at -4.3 ppm witnessed the presence of a four-coordinated boron center.



Scheme 5.1

An X-ray crystallographic study of **1a** confirmed the Lewis adduct structure (Figure 5.1). Of particular significance was the B-N bond length of 1.654(4) Å being slightly longer than that of the very stable piperidine-$B(C_6F_5)_3$ adduct (1.629(3) Å). This small bond elongation was however suspected to indicate the possibility of a thermal dissociation of the B-N bond. Indeed at 100 °C **1a** turned out to be thermally unstable in the presence of H_2 (1000 mbar) with the Lewis adduct partly dissociating into the "unquenched" donor and acceptor centers. Subsequent formation of a FLP and reaction with H_2 heterolysis affording the [**DMP**H][$HB(C_6F_5)_3$] salt **1b**. In the ^{1}H NMR spectrum **1b** featured a broad NH_2 resonance at 4.52 ppm accompanied by a broad quartet at 3.44 ppm with a *J*(B,H) coupling constant of 88 Hz. In addition, the narrowing gap between the *meta*- and *para*-fluorine ^{19}F NMR signals (-135.0 (*o*-), -162.5 (*p*-), -166.6 (*m*-C_6F_5) ppm) and a doublet ^{11}B NMR signal at -23.9 ppm were pointing to the formation of the tris(pentafluorophenyl)hydridoborate anion.

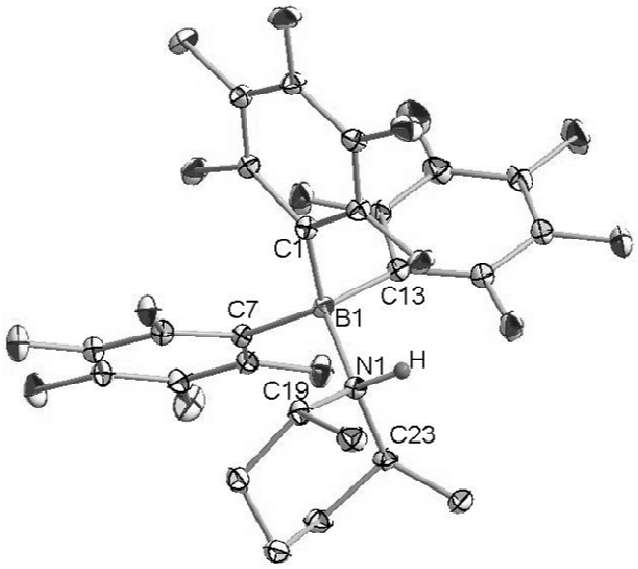


Figure 5.1 Molecular structure of ***1a*** *with 30% probability thermal ellipsoid. Hydrogen atoms are omitted for clarity.*

An X-ray diffraction analysis revealed in **1b** an elongated B-N distance of 3.949(2) Å with respect to **1a** (in agreement also with free rotation of the C_6F_5 rings in solution) and a H1···H2 separation of 1.945(1) Å, which could indicate a weak dihydrogen bonding

contact. The N1-H2 (1.01(4) Å) and N1-H3 (1.06(4) Å) bond lengths are longer than the N-H distance in **1a** (0.89(4) Å (N1-H)) (Figure 5.2).

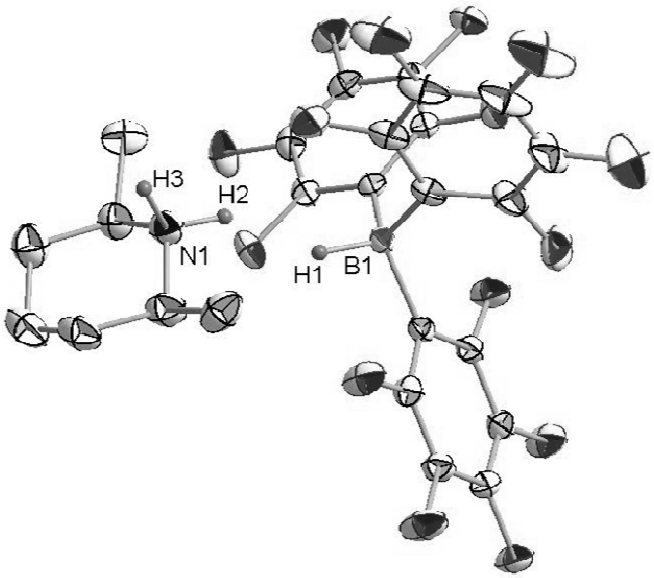


*Figure 5.2 Molecular structure of **1b** with 30% probability thermal ellipsoid. Hydrogen atoms are omitted for clarity.*

It is noteworthy that in the absence of H_2 dissociation of the **1a** Lewis pair did not become evident by spectroscopic or chemical means, for instance when heated to 110 ^{o}C for 20 h. Only trace amounts of the anion $[HB(C_6F_5)_3]^-$ were then formed as observed in the ^{19}F NMR and ^{11}B NMR spectra, which could originate from a $B(C_6F_5)_3$ induced α-hydride abstraction from **DMP** after rupture of the B-N bond similar to the chemistry leading to **4a** (Scheme 5.2), but the major part of the adduct remained intact.

From all these observations it was concluded that any kind of reaction of **1a** requires dissociation of the Lewis adduct at higher temperatures and the dissociated parts form a FLP, which in the presence or absence of H_2 can react further. The reaction barrier seems to be mainly due to the dissociation of the B-N bond and for instance the H_2 insertion and the H_2 splitting steps are without barrier. Nevertheless, this observation further proved that classic and frustrated Lewis pair reactivity are mutually not exclusive and previously "thought to be unreactive" classic Lewis acid-base adducts may be converted thermally to

Frustrated Lewis pairs offering thus access to new reactivity.

As Rieger et al. have reported, 2,2,6,6-tetramethyl-piperidine (**TMP**) exhibiting a still higher steric demand than **DMP** can heterolytically activate H_2 at room temperature in the presence of $B(C_6F_5)_3$.[23] To gain more quantitative insight and to trace intermediates a VT ^{1}H NMR study was carried out on this reaction in toluene solution starting at 193 K. A broad signal attributed to the H_B atom at 3.56 ppm was immediately observed after filling H_2 into the NMR tube containing the toluene solution of **TMP** and $B(C_6F_5)_3$ at 193 K (Figure 5.3, spectrum a). The N*H*$_2$ resonance appeared at this temperature as a quite broad signal at around 3.05 ppm. As the temperature was raised to 233 K, this broad signal became sharper and then gradually vanished with rising temperatures (Figure 5.3, spectra e-h). Initially, we thought this variable signal may be assigned to the H_2 enclosed FLP transient **TMP**$\cdots H^{\delta+}$-$H^{\delta-}\cdots B(C_6F_5)_3$. But continuing studies disproved this assumption and this signal was assigned to overlapping signals of N*H*(ax) and N*H*(eq) protons originating from a "frozen-out" chair conformation of the highly substituted piperidinium ring (see ground state conformations of the X-ray diffraction studies of **1b**, **2**, **3**, **4a**) in the temperature range between 193 K and 203 K. Assuming ring inversion at a rate comparable to the NMR time scale this signal at around 3 ppm coalesces at 213/223 K. At still higher temperatures the N*H*$_2$ signal gets sharper again (spectra e and f of Figure 5.3) with now signal averaging over various ring conformations fast on the NMR time scale. At still higher temperatures spectra g and h show that this resonance coalesces again, now due to fast proton exchange with the piperidine N*H* resonance, which was supposed to appear at around 0.5-1.5 ppm buried under the CH_3- and -CH_2- signals. The progressing H_2 splitting process produces an increasing amount of the piperidinium N*H*$_2$ moiety on the expense of the piperidine N*H* group shifting the N*H*/N*H*$_2$ averaged signal more and more to the piperidinium signal side as evidenced by the sequence of the ^{1}H NMR spectra a-f at 283 K of Figure 5.4. At the stage of spectra g and h the reaction is completed with the N*H*$_2$ signal of the piperidinuim cation appearing at 3.4 ppm. At this point also the signal of free H_2 gets visible, which during the progressing reaction was equilibrating with some yet unidentified resonance.

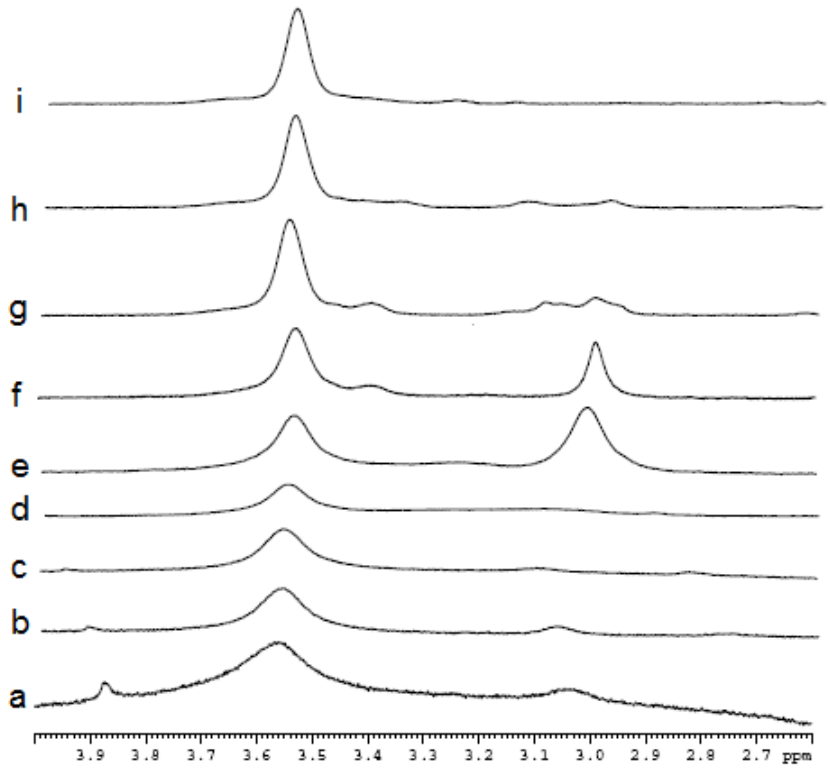


Figure 5.3 ***500*** *MHz VT* ^{1}*H NMR spectra of* ***TMP*** *and* $B(C_6F_5)_3$ *(1:1) with* H_2 *(1000 mbar) in* $[D_8]$*toluene. a: 193 K; b: 203 K, c: 213 K, d: 223 K, e: 233 K, f: 243 K, g: 253 K, h: 263 K, i: 273 K.*

Similar conclusions were drawn from a related VT ^{2}H NMR study of the splitting reaction of D_2 using **TMP** and $B(C_6F_5)_3$ with the decoalescing signals to expectedly appear at about 20 °C higher than in the case of the splitting reaction of H_2. The ^{2}H NMR spectra provided evidence for the position of the N*D* signal appearing temperature dependent in the range of 0.3 to 1.1 ppm. The reaction of the **TMP**/$B(C_6F_5)_3$ pair with HD was then carried out with VT ^{1}H NMR monitoring. The development of the spectra looked roughly similar to those of the H_2 experiments. We hoped to see resonances with *J*(HD) coupling patterns being attributable to an intact H-D connection, but no such signal was detected. All the given NMR pursuits pointed to the absence of a FLP/H_2 intermediate and it seemed therefore reasonable to assume that the splitting of the H_2 molecule occurs with no or almost no barrier. Within the given FLP model it was therefore anticipated that the

B···N distance of the **TMP**···$B(C_6F_5)_3$ encounter complex is too short to create a substantial NMR relevant barrier of > 12 kcal/mol.

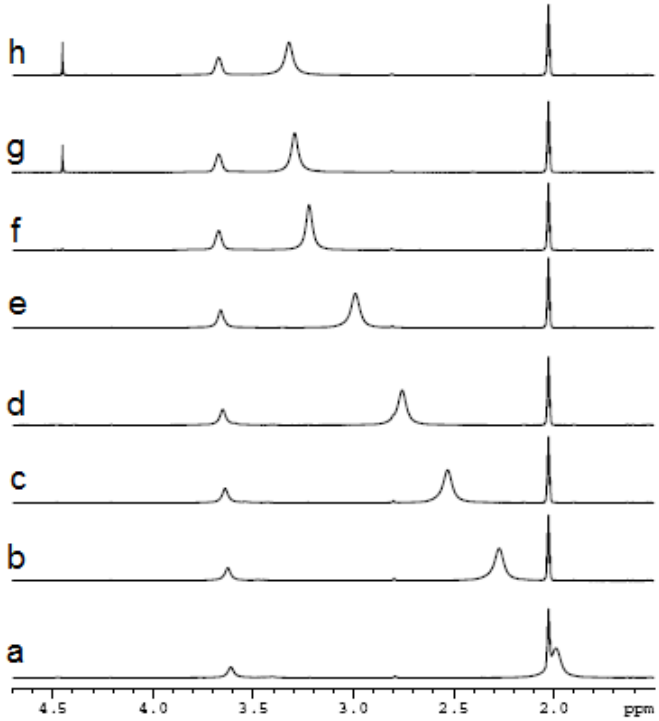


Figure 5.4 ***500*** *MHz* ^{1}*HNMR spectra (283 K) of TMP and* $B(C_6F_5)_3$ *(1:1) with* H_2 *(1000 mbar) in* $[D_8]$*toluene. a: start; b: after 2 h; c: after 4 h; d: after 6 h; e: after 8 h; f: after 10 h; g: after 12 h; h: after 14 h.*

The X-ray crystallographic study of **2** revealed a B-N distance of 4.565(3) Å setting the upper limit for a B···N distance in the corresponding FLP in solution. However, as we discussed in the earlier context the non-bonding B···N distance in the **TMP**···$B(C_6F_5)_3$ encounter complex should be longer than 4.5 Å to generate a substantial barrier in the H_2 activation and make the FLP/H_2 complex long-lived enough for spectroscopic characterization. It should also be mentioned that the H1A···H1 distance of 2.924(1) Å in the structure of **2** is too long for a dihydrogen bonding interaction (Figure 5.5).

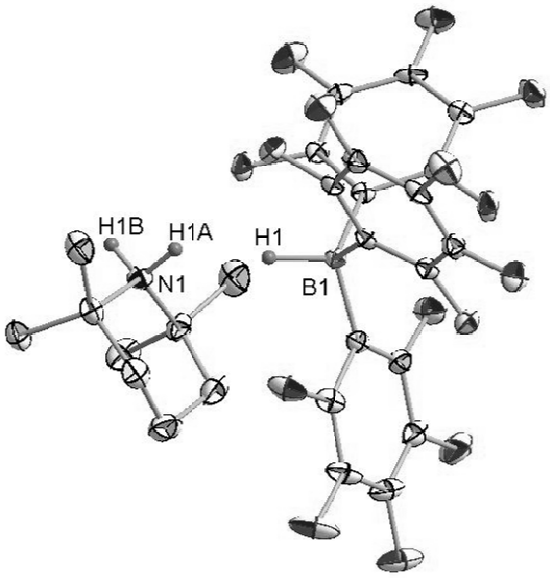


*Figure 5.5 Molecular structure of **2** with 30% probability thermal ellipsoid. Hydrogen atoms except NH and BH are omitted for clarity.*

In order to expand the B···N non-bonding distance of the B/N FLPs further, increase of the steric bulk around the N center was sought. Thus, we employed 1,2,2,6,6-pentamethylpiperidine (**PMP**) together with $B(C_6F_5)_3$ to react with H_2. The resulting reaction conditions for the H_2 heterolysis were expected to be much tougher in comparison with the **TMP**/$B(C_6F_5)_3$ system. ^{1}H NMR spectroscopy of the initial reaction solution in absence of H_2 at 193 K did not provide any evidence for the existence of a FLP intermediate. Only NMR resonances for the free components **PMP** and $B(C_6F_5)_3$ were observed and at 213 K the reaction with H_2 started to proceed revealing trace amounts of the product [**PMP**H][$HB(C_6F_5)_3$] **3**, but again no FLP/H_2 intermediate. At room temperature then the reaction went to completion within 1 h giving a 90 % yield of **3**. Thus, the **PMP**/$B(C_6F_5)_3$ reaction with H_2 required more severe reaction conditions confirming a higher energetic barrier to cleave the H_2 molecule than the **TMP**/$B(C_6F_5)_3$ system. The pure [**PMP**H][$HB(C_6F_5)_3$] product **3** featured in the ^{1}H NMR spectrum a broad N*H* resonance at 4.49 ppm. The ^{11}B NMR spectrum showed a doublet resonance at -18.5 ppm with a B-H coupling constant of 82 Hz, and in the ^{1}H NMR spectrum the corresponding H_B resonance was found at 3.78 ppm. Moreover, the relatively small Δδ(*m*-F)-(*p*-F)

separation was consistent with the presence of an anionic four-coordinate boron atom. A crystallographic study of **3** revealed face-to-face orientation of the [NH] and [BH] units with a H1···H2 separation of 2.191(1) Å (Figure 5.6) still in the range for dihydrogen bonding. It is interesting to see that the H1···H2 and B1···N1 (4.064 (2) Å) distances of **3** are both shorter than the corresponding ones of **2** indicating a closer packing of the ion pair. From this observation one might be inclined to predict a shorter B···N distance for the **PMP**···$B(C_6F_5)_3$ FLP and consequently a H_2 activation process without barrier, which however does not match with reality.

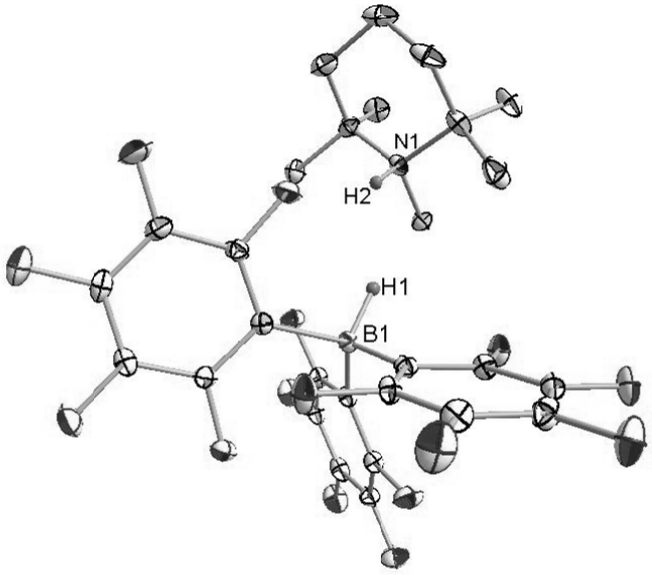


*Figure 5.6 Molecular structure of **3** with 30% probability thermal ellipsoid. Hydrogen atoms except NH and BH are omitted for clarity.*

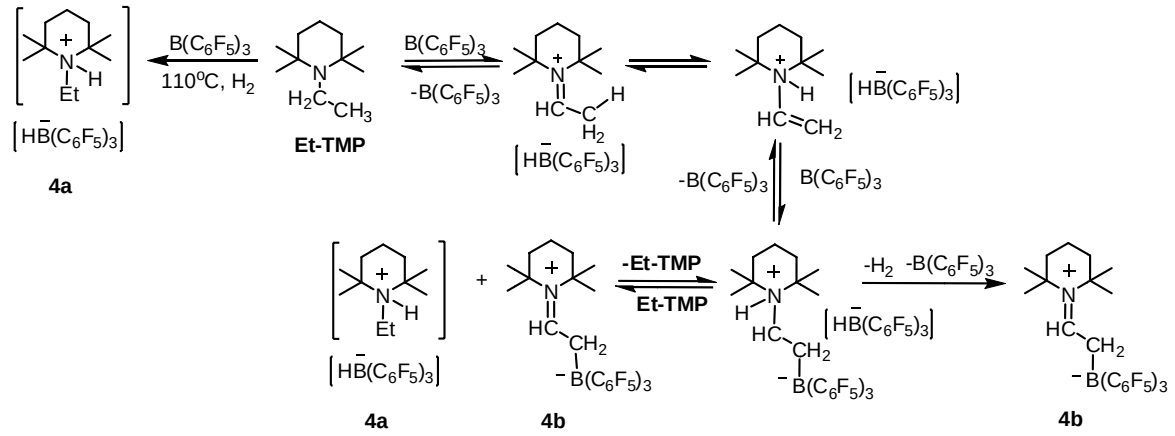
Enlarging the steric demand of the Lewis base further, 1-ethyl-2,2,6,6-tetramethylpiperidine (**Et-TMP**) was employed to increase within the given FLP model the distance to $B(C_6F_5)_3$. Indeed the mixture of **Et-TMP** and $B(C_6F_5)_3$ reacted in the presence of H_2 (1000 mbar) in benzene only at 110 °C to cleanly produce the H_2 split salt $[2,2,6,6\text{-}(CH_3)_4C_5H_6N(H)(CH_2CH_3)][HB(C_6F_5)_3]$ **4a** (Scheme 5.2). A still higher activation barrier was noticed in comparison with the **PMP**/$B(C_6F_5)_3$ reaction. This decrease in reaction rates might again be explained in the same way as for the given difference in reaction rates

between the **TMP**/$B(C_6F_5)_3$ and the **PMP**/$B(C_6F_5)_3$ pairs. In continuation of this series of sterically hindered piperidines as FLP base components, we also attempted preparation of a phenyl substituted **TMP** possessing no α-hydrogen. This endeavour however failed by many synthetic routes and was finally given up.

To conclude on this piperidine series for H_2 heterolysis we found increasing temperature limits for the reactions to proceed in follow the order: **TMP**(-80 °C) < **PMP**(25 °C) < **Et-TMP**(110 °C). This order is not in line with the extrapolated non-bonding B···N distances of the FLPs as derived from the X-ray structures of the products, the B/N ion pairs. This discrepancy let us assume that our structural extrapolation failed or other factors are to a significant extent responsible for the unexpected lower limits of the reaction temperatures of the piperidine···$B(C_6F_5)_3$ FLPs. To explain the above order of the piperidine···$B(C_6F_5)_3$ FLPs, one could among other possibilities assume on the basis of not too different FLP association energies decreasing FLP associations with increasing temperatures and consequently lowered actual FLP concentrations at higher reaction temperatures, which are anticipated to lead to reduced overall reaction rates.

It was intriguing to see that in the absence of H_2 the stoichiometric mixture of **Et-TMP** and $B(C_6F_5)_3$ reacted giving **4a** and [2,2,6,6-$(CH_3)_4C_5H_6N$=$CHCH_2$-$B(C_6F_5)_3$] **4b** in a ratio of about 3:7 based on the NMR spectroscopic analysis (Scheme 5.2). **4b** featured a =C*H* resonance at 8.07 pm and a =CH-CH_2 resonance of 3.17 ppm in the ^{1}H NMR spectrum. In addition, the ^{19}F NMR resonances at -133.5 (*o*-), -160.8 (*p*-), -165.7 ppm (*m*-C_6F_5) and a singlet at -13.9 ppm in the ^{11}B NMR spectrum were consistent with the formation of a four-coordinate boron anion. A single crystal X-ray diffraction analysis of **4b** revealed a *transoid* structure of the [2,2,6,6-$(CH_3)_4C_5H_6N$=$CHCH_2$-$B(C_6F_5)_3$] molecule in the solid state with a N1····B1 non-bonding distance of 3.865(1) Å (Figure 5.7).

So, in absence of H_2, the Lewis acid $B(C_6F_5)_3$ actually effected *α*-hydride abstraction from the **Et-TMP** molecule, which might indicate that the B···N distance in the **Et-TMP**···$B(C_6F_5)_3$ FLP could be shorter than compared to those in the **PMP**···$B(C_6F_5)_3$ or **TMP**···$B(C_6F_5)_3$ encounter complexes, because the reactants had to come even very close to initiate *α*-hydride abstraction. A similar reaction as for the **Et-TMP**/$B(C_6F_5)_3$ was observed between bulky



Scheme 5.2

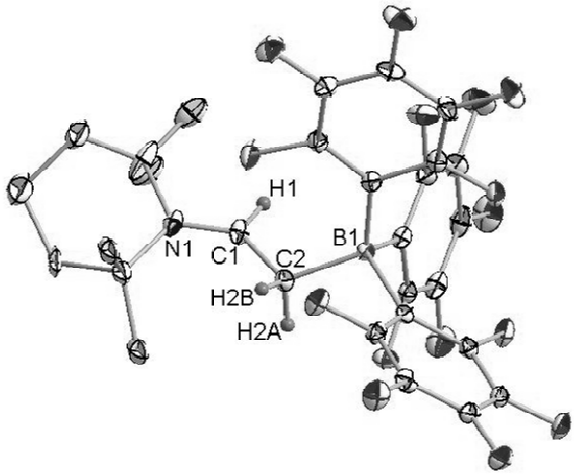


Figure 5.7 Molecular structure of ***4b*** *with 30% probability thermal ellipsoid. Hydrogen atoms except C1 and C2 are omitted for clarity.*

amines and $B(C_6F_5)_3$,[23,30-32] and by analogy the reaction of the trityl cation with sterically hindered amines afforded also an iminium cation rather than formation of a FLP with subsequent typical reactivity.[33] Subsequent to the α-hydride abstraction of **Et-TMP** the intermediate $[2,2,6,6\text{-}(CH_3)_4C_5H_6N{=}CHCH_3]$ $[HB(C_6F_5)_3]$ was envisaged to undergo a 1,3-H-shift to the vinyl ammonium salt $[2,2,6,6\text{-}(CH_3)_4C_5H_6NH\text{-}CH{=}CH_2][HB(C_6F_5)_3]$ (Scheme 5.2). The remaining Lewis acid $B(C_6F_5)_3$ then attacked the β-carbon atom of the cation and promoted proton transfer to a base from the acidic N*H* function to yield **4b**. The released proton was accepted either by free **Et-TMP** affording

$[2,2,6,6\text{-}(CH_3)_4C_5H_6N(H)CH_2CH_3][HB(C_6F_5)_3]$ **4a** or reacted with the anion $[HB(C_6F_5)_3]^-$ as a base to generate H_2 and free $B(C_6F_5)_3$, the latter could re-enter reactions as a starting material.

Interestingly, at 110 °C the reaction of **4a** and **4b** got reversed within 24 h and in the presence of H_2 **4a** was formed in a total yield of more than 80%. In the initial mixture **4a** is thus proposed to act as a proton and hydride transfer reagent ("ionic hydrogenation" conditions)[34] to the iminium α- and β-carbon regenerating **Et-TMP** and $B(C_6F_5)_3$, which could then in a FLP type reaction activate H_2 heterolytically producing **4a** (Scheme 5.2). In C_6D_6 solution **4a** showed two sets of ^{19}F NMR signals (-134.1. -164.5, -167.7 and -134.4, -165.5, -168.4 ppm) in an approximate 1:1 ratio attributed to the *o*-, *p*-, *m*-substituent fluorine atoms, which indicated two different arrangements of the ions, ion paired structures based on slowly inverting axial and equatorial positions of the Et substituent. In the crystal of **4a** the equatorial "ion pair" seemed to prevail (*vide infra*). The ion paring is supposed to stabilize these conformers each in its own way. The polar solvent $CDCl_3$ prevented formation of ion pairs by solvation effects, thus only the free ions of **4a** with an piperidinium ring inverting fast on the NMR timescale could be identified which exhibited ^{19}F NMR resonance at -134.8 (*o*-), -164.5 (*p*-), -167.8 (*m*-C_6F_5) ppm in $CDCl_3$ solution.

The single crystal X-ray diffraction study of **4a** revealed that the cation and anion are oriented face-to-face toward each other. The H1···H2 and B1···N1 non-bonding distances amount to 3.88(1) Å and to 5.38(2) Å, respectively (Figure 5.8). These separations are quite long as compared to those in **2** and **3**, but seemed not particularly meaningful in terms of a retrospective estimate of the FLP distance from which **4a** was assumed to be formed.

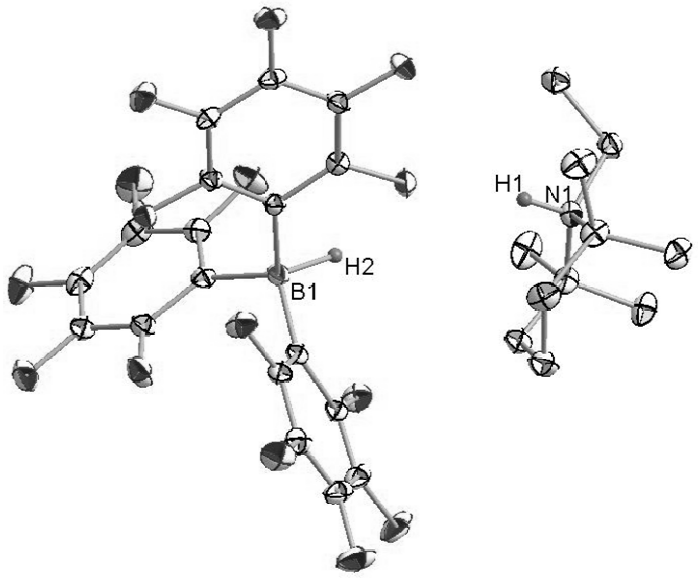
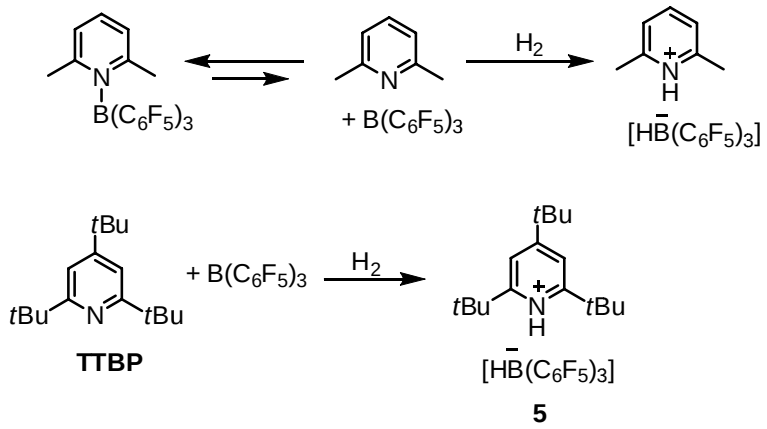


Figure 5.8 Molecular structure of ***4a*** *with 30% probability thermal ellipsoid. Hydrogen atoms except NH and BH are omitted for clarity.*

Lutidine (**LUT**) shows lower basicity compared to piperidine. It has been reported to exhibit "border" reactivity of classical and frustrated Lewis pair properties with $B(C_6F_5)_3$ at room temperature.[35] We repeated the reaction at 25°C in toluene solvent and tried to trace the intermediacy of the FLP/H_2 complex in the H_2 splitting process via ^{1}H NMR and ^{11}B NMR pursuits, but could not find any hint to the existence of intermediates. In the ^{11}B NMR spectrum at room temperature in toluene solution a singlet and a doublet at -4.5 and -25.2 ppm indicated the formation of the classical Lewis adduct (2,6-$Me_2C_5H_3N$)$B(C_6F_5)_3$ and the ionic product [2,6-$Me_2C_5H_3NH$][$HB(C_6F_5)_3$], which were similar to those found by Stephan.

We also tested the pyridine derivative, 2,4,6-tri-tert-butylpyridine (**TTBP**), as a Lewis base (Scheme 5.4). In combination with $B(C_6F_5)_3$ it was capable of activating H_2 heterolytically at 1 bar pressure at room temperature, but it required 24 h to reach a yield of 80 %. The isolated product [**TTBP**H][$HB(C_6F_5)_3$] **5** features a broad N*H* resonance at 10.8 ppm and a quartet signal at 3.56 ppm for the B*H* atom with a $J_{B\text{-}H}$ coupling constant of 90 Hz. The ^{19}F NMR spectrum showed signals at δ -135.2 (*o*-), -165.6 (*p*-), -168.9 (*m*-C_6F_5) ppm consistent with the pseudo-tetrahedral boron atom of the anion. This was

also confirmed via the X-ray structure (Figure 5.9), which is the same as the previously reported structure.[36] The B1···N1 non-bonding distance in the solid state is 4.78 (2) Å and the H1···H2 distance was found to be 3.51(1) Å. Both lengths witness isolated ions rather than a contact ion pair.



Scheme 5.4

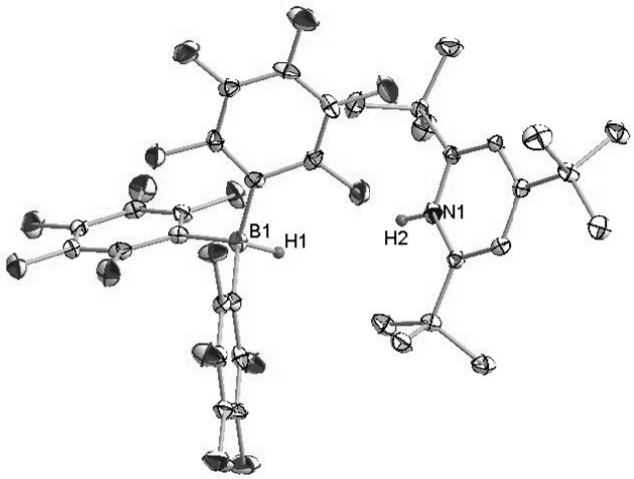


Figure 5.9 Molecular structure of **5** *with 30% probability thermal ellipsoid. Hydrogen atoms except NH and BH are omitted for clarity.*

Based on the FLP concept we attempted quantification of the steric influence of the Lewis bases by attributing them a cone angle derived from their adduct with $B(C_6F_5)_3$ (or with BH_3 for **PMP** and **Et-TMP**). A B-N bond distance of 1.7 Å was used in the DFT calculations of

the cone angles (Table 1). The **DMP** showed relatively small cone angles of 152°, which nicely mirrors the fact that it forms a Lewis adduct with $B(C_6F_5)_3$. The **LUT** possess a cone angle of 164°, which together with $B(C_6F_5)_3$ led to an equilibrium between free **LUT**/$B(C_6F_5)_3$ and the Lewis acid-base adduct at room temperature. According to the calculation results the **TTBP**'s cone angle (166°) is only a little larger than for **LUT**, but no Lewis adduct was observed only FLP chemistry in the presence of $B(C_6F_5)_3$. This might demonstrate that the Lewis adduct formation is reacting to even small changes in the cone angles, while FLP reactivity demands first of all the free Lewis pair and in a secondary way influences the FLP reactivity. **TMP** and **TTBP** bases have similar cone angles, as assumption, they should have the similar B···N distance in the FLP encounter complexes. The quite fast reaction between **TMP**···$B(C_6F_5)_3$ and H_2 in comparison with **TTBP**···$B(C_6F_5)_3$ case is presumably also due to the much stronger Lewis basicity of **TMP**, which causes a high electrostatic field in the FLP cage.[28] Comparing the cone angles of **TMP** and **PMP**, the B···N distance in the **PMP**···$B(C_6F_5)_3$ FLP seemed to be necessarily longer than in the **TMP**···$B(C_6F_5)_3$ one, which might explain why **PMP**···$B(C_6F_5)$ FLP requires severer reaction condition to activate H_2. Nevertheless, the picture derived from non-bonding B···N distance in the crystal structures of the H_2 splitting products gave a different order. This might be explained with a considerable

Table 1. Cone angles* for piperidine and pyridine derivatives (°)

Compound	Cone angle
2,6-dimethylpiperidine (**DMP**)	152
2,2,6,6-tetramethylpiperidine (**TMP**)	169
1,2,2,6,6-pentamethylpiperidine (**PMP**)	194
1-ethyl-2,2,6,6-tetramethylpiperidine (**Et-TMP**)	203
2,6-lutidine (**LUT**)	164
2,4,6-tri-tert-butylpyridine (**TTBP**)	166

*Cone angles of the piperidine and pyridine derivatives X based on the DFT-optimized geometries of X-$B(C_6F_5)_3$ (or X-BH_3 for X = **PMP** and **Et-TMP**). A fixed B-N bond distance of 1.7 Å was used in the calculations of the cone angles.

structural flexibility of the bases in the encounter complexes. **Et-TMP**, though has a larger cone angle than **PMP**, but reaction course with the α-hydride abstraction by $B(C_6F_5)_3$ suggested the possibility of a closer B···N contact in the transition state being presumably related to the "frustration" state. Thus, the cone angle determination combined with the experimental evidence point to a great structural flexibility in the FLP, which would not easily allow to take B···N distance as the decisive parameter for FLP reactivity.

Conclusion

We applied several pyridine and piperidine derivatives to find correlations between the bulk of Lewis bases in FLP contact with $B(C_6F_5)_3$ and their reactivity in heterolytic H_2 activation. **DMP** with $B(C_6F_5)_3$ forms a classical Lewis pair. The Lewis acid combines with the Lewis base resulting in the adduct **DMP**-$B(C_6F_5)_3$ at low temperature; but at higher temperature of 110 ^oC, this pair dissociates forming the encountering FLP, which then can activate H_2 heterolytically. The sterically demanding **TMP**, **PMP** and **Et-TMP** together with $B(C_6F_5)_3$, however, formed encounter complexes, which apparently activated the H_2 molecule without barrier. Especially the **TMP**···$B(C_6F_5)_3$ system was found capable of splitting H_2 even at 193 K. The strong Lewis acid $B(C_6F_5)_3$ encountered with the sterically highly demanding amine ethyltetramethylpiperidine (**Et-TMP**) underwent in the absence of H_2 hydride abstraction of the α-H. After a 1,3-H-shift a vinyl ammonium cation was formed, which adds $B(C_6F_5)_3$ at the C_β atom. Its acidified character promotes deprotonation of the H_N atom by bases present in the reaction mixture, either the $[HB(C_6F_5)_3]^-$ anion or **Et-TMP**. Pyridine derivatives exhibit weaker Lewis basicity compared to piperidine derivatives, but still possess the ability to activate H_2 with $B(C_6F_5)_3$ under certain reaction conditions. Our studies suggest that the FLPs have the characteristic feature of structural flexibility allowing variation of the B···N distance in a quite broad range. Whether or not this distance or the bases' cone angles would have influence on the FLP reactivity, could not be unravelled by these studies. In addition, detection of LB···H_2···LA intermediates through variation of the bases' cone angles

remains to be a challenge.

Experimental part

General consideration: All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze-thaw cycles prior to use. **DMP**, **TMP**, **PMP**, **LUT** and **TTBP** were purchased from Aldrich and stored over molecular sieves. $B(C_6F_5)_3$ were prepared according to the literature.[36] ^1H NMR, ^{19}F NMR, $^{11}B\{^1H\}$ NMR data were recorded on a Varian Gemini-300 spectrometer. Chemical shift are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F, ^{11}B were referenced to $CFCl_3$, BF_3OEt_2, respectively. Microanalyses were carried out at the Anorganisch-Chemisches Institute of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoK_α radiation, λ = 0.71073 Å).[37] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction[38] and data reduction were performed with the Oxford program suite *CrysAlisPro*.[39] The structures were solved with the direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[40] All programs used during the crystal structure determination process are included in the WINGX software.[41] The program PLATON[42] was used to check the results of the X-ray studies and to analyze the hydrogen-bonding systems. The hydrogen atoms bound to nitrogen or phosphorus were located in a difference Fourier map and refined without restraints. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C-H distances in the range 0.93 – 0.97 Å and their isotropic displacement parameters constrained to $1.2U_{eq}(C)$ or $1.5U_{eq}(C)$.

Synthesis of Et-TMP

2,2,6,6-tetramethyl-piperidine (**TMP**) (2.82 g, 20 mmol) and K_2CO_3 (3.45 g, 25 mmol) and 5 mL of CH_3CN were added to a 50mL round-bottom flask. The mixture was refluxed for 1 h at 85 ^oC in an oil bath with continuous stirring, after that the CH_3CH_2I (3.12 g, 20 mmol) was added to the mixture. The mixture was refluxed for additional 2 days and then cooled to room temperature. After the filtration, the solvent was removed under vacuum with the formation of viscous liquid. The product was purified by silica gel flash column chromatography, eluting with an ethyl acetate/hexane mixture (1:20 v/v). The fraction containing the product was collected after removing the solvent *in vacuo*, Yield: 65 %. The product **Et-TMP** was stored over molecular sieves. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 0.93 (s, 12H, CH_3), 1.00 (t, 3H, $^3J_{HH}$ = 6 Hz, CH_3), 1.32 (m, 4H, CH_2), 1.38 (m, 2H, CH_2), 2.33 (q, 2H, $^3J_{HH}$ = 6 Hz, CH_2).

Preparation of DMP-B(C_6F_5)$_3$ 1a

$B(C_6F_5)_3$ (0.013 g, 0.025 mmol) and 2,6-dimethylpiperidine (**DMP**) (0.0028g, 0.025 mmol) were dissolved in C_6D_6 (0.5 mL) giving a colorless solution. The solution was characterized by NMR spectroscopy. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 0.54 (m, 2H, -CH_2), 0.71 (m, 2H, -CH_2) 0.87 (d, 6H, $^3J_{HH}$ = 6 Hz, -CH_3), 3.42 (m, 2H, -CH), 5.35 (br, 1H, N*H*). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -4.3 (s). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -128.2 (br, 2F, *o*-C_6F_5), -128.5 (d, 2F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -138.6 (br, 2F, *o*-C_6F_5), -155.2 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -157.6 (t, 2F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -162.4 (br, 2F, *m*-C_6F_5), -164.4 – -164.6 (m, 4F, *m*-C_5F_5). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz, 293 K): δ 149.7 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5), 139.4 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *p*-C_6F_5), 136.3 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *m*-C_6F_5), 51.7 (*o*-C_5H_9N), 26.5 (*m*-C_5H_9N), 22.8 (CH_3), 10.8 (*p*-C_5H_9N). Anal.Calcd. for $C_{25}H_{15}BF_{15}N$: C, 48.03; H, 2.42; N, 2.24. Found: C, 48.20; H, 2.47; N, 2.18.

X-ray Crystal Structure Analysis of **1a**: formula $C_{25}H_{15}BF_{15}N$, *M*r = 625.19, Orthorhombic, $Pca2_1$, *a* = 17.8991(4) Å, *b* = 9.0917(2) Å, *c* = 14.4468(3) Å, *V* = 2350.97(9) Å^3, *Z* = 4, *Dc* = 1.766 g cm^{-3}, μ = 0.186 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 23274 reflections collected, 3713

independent (R_{int} = 0.0710) and 2972 observed reflections ($I > 2\sigma(I)$), 385 refined parameters, R_1 = 0.0431, wR_2 = 0.1027. CCDC 698951.

Preparation of [DMPH][HB(C_6F_5)$_3$] 1b

Solid B(C_6F_5)$_3$ (0.256 g, 0.5 mmol) and 2,6-dimethylpiperidine (**DMP**) (0.0566 g, 0.5 mmol, 0.067mL) were added to the a 50 mL Schlenk tube and dissolved in toluene (10 mL) giving a colorless solution. The Schlenk tube was filled with H_2 (1000 mbar) and the solution was allowed to stir at 110 ^oC for 20 h, there was no precipitation formed during this period of time. Then the solvent was removed under reduced pressure and a white solid was obtained, which then was washed with pentane. The product was collected as a white solid. Yield: 71%. ^1H NMR (C_6D_6, 300 MHz, 293 K): δ 0.35 (m, 4H, -CH_2), 0.52 (d, 6H, $^3J_{HH}$ = 6 Hz, -CH_3), 0.72 (m, 2H, -CH_2), 2.01 (br, 2H, -CH), 3.44 (q, 1H, $^1J_{HB}$ = 88 Hz, -B*H*), 4.52 (br, 2H, -N*H*). ^{11}B {^1H} NMR (C_6D_6, 96 MHz, 293 K): δ -23.9 (s). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -135.0 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -162.5 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -166.6 (t, 6F, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5). ^{13}C {^1H} NMR (C_6D_6, 75 MHz, 293 K): δ 148.8 (dm, $^1J_{C\text{-}F}$ = 248 Hz, *o*-C_6F_5), 139.1 (dm, $^1J_{C\text{-}F}$ = 250 Hz, *p*-C_6F_5), 137.3 (dm, $^1J_{C\text{-}F}$ = 247 Hz, *m*-C_6F_5), 56.7 (*o*-C_5H_9N), 29.6 (*m*-C_5H_9N), 22.7 (CH_3), 18.8 (*p*-C_5H_9N). Anal.Calcd. for $C_{25}H_{17}BF_{15}N$: C, 47.87; H, 2.73; N, 2.23. Found: C, 47.92; H, 2.54; N, 2.10.

X-ray Crystal Structure Analysis of **1b**: formula $C_{63}H_{48}B_2F_{30}N_2$, *M*r = 1424.65, Monoclinic, $P2_1/n$, a = 12.3238(2) Å, b = 16.6160(2) Å, c = 15.7963(2) Å, β = 107.804(2)°, V = 3079.73(8) Å^3, Z = 2, Dc = 1.536 g cm^{-3}, μ = 0.153 mm^{-1}, λ = 0.71073 Å, T = 183(2) K, 41687 reflections collected, 6301 independent (R_{int} = 0.0281) and 4570 observed reflections ($I > 2\sigma(I)$), 443 refined parameters, R_1 = 0.0632, wR_2 = 0.1755. CCDC 790973.

Preparation of [TMPH][HB(C_6F_5)$_3$] 2

Solid B(C_6F_5)$_3$ (0.256g, 0.5mmol) and 2,2,6,6-tetramethyl-piperidine (**TMP**) (0.0705g, 0.5mmol) were added to a 50mL Schlenk tube and dissolved in toluene (10 mL) giving a colorless solution. The Schlenk tube was filled with H_2 (1000 mbar) and the solution was allowed to stir at room temperature for 30 min. Then the solvent was removed applying vacuum. The remaining white solid was washed with hexane. Yield: 91%. ^1H NMR

(toluene-d_8, 300 MHz, 293 K): δ 0.54 (s, 12H, -CH_3), 0.66 (m, 4H, CH_2), 0.76 (m, 2H, CH_2), 3.61 (q, 1H, $^1J_{H\text{-}B}$ = 90 Hz, B*H*), 4.32 (br, 2H, N*H*). ^{11}B {^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ -20.3 (s). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ -135.3 (d, 6F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -164.2 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -168.0 (t, 6F, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5). ^{13}C {^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 149.4 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5), 139.6 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *p*-C_6F_5), 137.9 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *m*-C_6F_5), 59.6 (*o*-C_5H_7N), 33.7 (*m*-C_5H_7N), 26.5 (CH_3), 14.9 (*p*-C_5H_7N). Anal.Calcd. for $C_{27}H_{21}BF_{15}N$: C, 49.49; H, 3.23; N, 2.14. Found: C, 49.60; H, 3.34; N, 2.18.

X-ray Crystal Structure Analysis of **2**: formula $C_{27}H_{21}BF_{15}N$, *M*r = 655.26, Orthorhombic, $P2_12_12_1$, *a* = 11.0986(3) Å, *b* = 13.9205(3) Å, *c* = 17.7055(4) Å, *V* = 2735.47(11) Å^3, *Z* = 4, *Dc* = 1.591 g cm^{-3}, μ = 0.164 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 20210 reflections collected, 4615 independent (R_{int} = 0.0206) and 3362 observed reflections ($I > 2\sigma(I)$), 413 refined parameters, R_1 = 0.0345, wR_2 = 0.0772. CCDC 698950.

Preparation of [PMPH][HB(C_6F_5)$_3$] 3

B(C_6F_5)$_3$ (0.1024 g, 0.2 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.031 g, 0.2 mmol) were added to a 50 mL Schlenk tube and dissolved in toluene (5 mL) giving a yellow solution. The Schlenk tube was filled with H_2 (1000 mbar) and the solution was allowed to stir at r.t. for 2 h. There was no precipitate formed during this process. The reaction was then concentrated to half of its volume and hexane was added to induce precipitation. The product was washed with hexane after filtration and dried *in vacuo*. Yield: 82 %. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 0.28 (s, 6H, CH_3), 0.57 (s, 6H, CH_3), 0.84 (m, 4H, CH_2), 1.08 (m, 2H, CH_2), 1.80 (d, 3H, $^3J_{HH}$ = 6 Hz, N-CH_3), 3.78 (q, 1H, $^1J_{HB}$ = 82 Hz, B*H*), 4.49 (br, 2H, N*H*). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ -134.3 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -163.6 (t, 3F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -167.3 (t, 6F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). ^{11}B {^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ -18.5 (s). ^{13}C {^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 148.2 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *o*-C_6F_5), 138.7 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *p*-C_6F_5), 137.3 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *m*-C_6F_5), 65.6 (*o*-C_5H_6N), 37.5 (*m*-C_5H_6N), 29.1 (CH_3), 18.8 (N-*C*H_3), 15.2

(*p*-C_5H_6N). Anal.Calcd. for $C_{28}H_{23}BF_{15}N$: C, 50.25; H, 3.46; N, 2.09. Found: C, 50.52; H, 3.32; N, 1.90.

X-ray Crystal Structure Analysis of **3**: formula $C_{28}H_{23}BF_{15}N$, *M*r = 669.28, Triclinic, P -1, *a* = 10.7424(1) Å, *b* = 11.2219(1) Å, *c* = 13.6153(1) Å, α = 81.196(1)°, β = 72.844(1)°, γ = 63.415(1)°, *V* = 1402.06(3) Å^3, *Z* = 2, *Dc* = 1.585 g cm^{-3}, μ = 0.162mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 30255 reflections collected, 8556 independent (R_{int} = 0.0248) and 5955 observed reflections ($I > 2\sigma(I)$), 419 refined parameters, R_1 = 0.0396, wR_2 = 0.1049. CCDC 790974.

Preparation of [2,2,6,6-$(CH_3)_4$-$C_5H_6NH(CH_2CH_3)$][$HB(C_6F_5)_3$] 4a and [2,2,6,6-$(CH_3)_4$-C_5H_6N=$CHCH_2$-$B(C_6F_5)_3$] 4b

$B(C_6F_5)_3$ (0.1024 g, 0.2 mmol) and 1-Ethyl-2,2,6,6-pentamethylpiperidine (0. 034 g, 0.2 mmol) were added to a 50 mL Schlenk and dissolved in toluene (5 mL) giving a yellow solution. After stirring for 10 mins at r.t., the reaction was then concentrated to half volume and hexane was added to promote precipitation. The product was washed with hexane after filtration and dried *in vacuo*. The white product contains the mixture of **4a** and **4b** in approximate 3:7. Yield: 82 %. **4b**: ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 0.47 (s, 6H, -CH_3), 0.72 (s, 6H, -CH_3), 0.89 (m, 4H, -CH_2), 1.25 (m, 2H, -CH_2), 3.17 (br, 2H, =CH-CH_2), 8.07 (br, 1H, =C*H*-CH_2). ^{11}B {^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -13.9 (s). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -133.5 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -160.8 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -165.7 (t, 6F, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5).

X-ray Crystal Structure Analysis of **4b**: formula $C_{29}H_{21}BF_{15}N$, *M*r = 679.28, Monoclinic, C2/c, *a* = 23.0895(3) Å, *b* = 11.0393(2) Å, *c* = 21.5309(3) Å, β = 90.593(1)°, *V* = 5487.76(14) Å^3, *Z* = 8, *Dc* = 1.644 g cm^{-3}, μ = 0.167 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 26356 reflections collected, 6799 independent (R_{int} = 0.0216) and 4967 observed reflections ($I > 2\sigma(I)$), 435 refined parameters, R_1 = 0.0460, wR_2 = 0.1254. CCDC 790976.

Preparation of [2,2,6,6-$(CH_3)_4$-$C_5H_6NH(CH_2CH_3)$][$HB(C_6F_5)_3$] 4a

Solid $B(C_6F_5)_3$ (0.1024 g, 0.2 mmol) and 1-Ethyl-2,2,6,6-pentamethylpiperidine (0. 034 g, 0.2 mmol) were added to a 50mL Schlenk and dissolved in toluene (5 mL) giving a colorless solution. The solution was filled with H_2 (1000 mbar) and the solution was allowed to stir at

110 °C for 24 h, there was no precipitate formed during this process. The reaction was then concentrated to half of its original volume and pentane was added to induce precipitation. The product was washed with pentane after filtration and dried *in vacuo*. The product was collected as a white solid. Yield: 81%. ^{1}H NMR (C_6D_6, 300 MHz, 293 K): δ 0.28 (s, -CH_3), 0.39 (s, -CH_3), 0.46 (s, -CH_3), 0.52 (s, -CH_3), 0.55 (t, $^3J_{HH}$ = 6 Hz, -CH_2-C*H*$_3$), 0.64 (t, $^3J_{HH}$ = 6 Hz, -CH_2-C*H*$_3$), 0.86 (m, -CH_2), 1.91 (m, -C*H*$_2$-CH_3), 2.03 (m, -C*H*$_2$-CH_3), 2.37 (br, B*H*), 4.24 (br, N*H*). ^{19}F NMR (C_6D_6, 282 MHz, 293 K): δ -134.1 (d, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -134.4 (d, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -164.5 (t, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -165.5 (t, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), -167.7 (t, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5), -168.4 (t, $^3J_{FF}$ = 21 Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -25.1 (s).

^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.46 (s, 6H, -CH_3), 1.53 (s, 6H, -CH_3), 1.56 (t, 3H, $^3J_{HH}$ = 6 Hz, -CH_2-C*H*$_3$), 1.86 (qd, 2H, J_{HH} = 6, 3 Hz, -C*H*$_2$-CH_3), 3.51 (br, B*H*), 4.00 (br, N*H*). ^{19}F NMR ($CDCl_3$, 282 MHz, 293 K): δ -134.8 (d, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5), -164.5 (t, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -167.8 (t, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{11}B{^{1}H} NMR (C_6D_6, 96 MHz, 293 K): δ -25.2 (s).

X-ray Crystal Structure Analysis of **4a**: formula $C_{29}H_{25}BF_{15}N$, *M*r = 683.31, Monoclinic, $P2_1$, *a* = 10.2209(6) Å, *b* = 15.4745(6) Å, *c* = 10.1157(6) Å, β = 114.872(7)°, *V* = 1451.54(16) Å^3, *Z* = 2, *Dc* = 1.563 g cm^{-3}, μ = 0.158 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 23737 reflections collected, 3742 independent (R_{int} = 0.0365) and 3418 observed reflections ($I > 2\sigma(I)$), 426 refined parameters, R_1 = 0.0356, wR_2 = 0.1002. CCDC 790975.

Preparation of [TTBPH][HB(C_6F_5)$_3$] 5

Solid B(C_6F_5)$_3$ (0.256 g, 0.5 mmol) and 2,4,6-tri-tert-butylpyridine (0.123 g, 0.5 mmol) were added to the a 50mL Schlenk and dissolved in toluene (10 mL) giving a colorless solution. The solution was filled with H_2 (1000 mbar) and the solution was allowed to stir at room temperature for 24 h, there was no precipitate formed during this process. Then solvent was removed through reduced pressure to leave behind a white solid, which was then washed with hexane and diethyl ether. The product was collected as a white solid. Yield: 80 %. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 1.39 (s, 9H, *p*-*t*Bu), 1.50 (s, 18H, *o*-*t*Bu), 3.56 (q, 1H,

$^1J_{H\text{-}B}$ = 90 Hz, B*H*), 7.78 (s, 2H, C_5H_2N), 10.8 (br, 1H, N*H*). ^{11}B {^1H} NMR (CD_3CN-d3, 96 MHz, 293 K): δ -24.59 (d, $^1J_{H\text{-}B}$ = 90 Hz). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ -135.2 (d, 6F, $^3J_{FF}$ = 18 Hz, o-C_6F_5), -165.6 (t, 3F, $^3J_{FF}$ = 20 Hz, p-C_6F_5), -168.9 (t, 6F, $^3J_{FF}$ = 25 Hz, m-C_6F_5). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz, 293 K): δ 163.7 (*o*-C_5H_2N), 151.0 (*p*-C_5H_2N), 147.8 (*o*-C_6F_5), 139.3 (*p*-C_6F_5), 136.0 (*m*-C_6F_5), 120.7 (*m*-C_5H_2N), 37.9 (*o*-$C(CH_3)$), 37.7 (*p*-$C(CH_3)$), 30.2 (*p*-$C(CH_3)$), 29.0 (*o*-$C(CH_3)$). Anal. Calcd for $C_{35}H_{31}BF_{15}N$: C, 55.21; H, 4.10; N, 1.84. Found: C, 55.60; H, 4.18; N, 1.87.

X-ray Crystal Structure Analysis of **5**: formula $C_{38}H_{38}BF_{15}N$, *M*r = 804.50, Triclinic, P-1, a = 9.8216(3) Å, b = 10.7921(3) Å, c = 18.7474(6) Å, α = 74.768(3)°, β = 77.215(3)°, γ = 78.314(3)°, V = 1847.65(10) Å^3, Z = 2, Dc = 1.446 g cm^{-3}, μ = 0.136 mm^{-1}, λ = 0.71073 Å, T = 183(2) K, 19560 reflections collected, 6995 independent (R_{int} = 0.0421) and 3529 observed reflections ($I > 2\sigma(I)$), 514 refined parameters, R_1 = 0.0495, wR_2 = 0.1148. CCDC 736260.

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Activation of Terminal Alkynes by Frustrated Lewis Pairs

Abstract

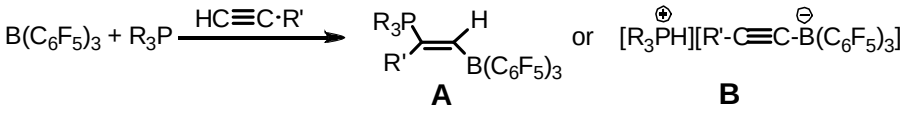
The reaction of frustrated Lewis pairs (FLPs) derived from $B(C_6F_5)_3$ and bulky Lewis bases 2,2,6,6-tetramethylpiperidine (**TMP**), tri-*tert*-butylphosphine, lutidine (**Lut**) with terminal alkynes (acetylene, phenylacetylene, 3-ethynylthiophene) were investigated. The FLPs **TMP**$\cdots B(C_6F_5)_3$, *t*-$Bu_3P\cdots B(C_6F_5)_3$ and **Lut**$\cdots B(C_6F_5)_3$ reacted with acetylene (HC≡CH) to yield the apparently thermodynamically more stable *E* isomers [**TMP**H][$(C_6F_5)_2$B-C(C_6F_5)=C(H)B$(C_6F_5)_3$] **1-*E***, *t*-Bu_3PC(H)=C(H)B$(C_6F_5)_3$ (90 %) **2a-*E*** and [*t*-Bu_3PH][$(C_6F_5)_2$B-C(C_6F_5)=C(H)B$(C_6F_5)_3$] (10 %) **2b-*E*** and **Lut**C(H)=C(H)B$(C_6F_5)_3$ **3-*E***, respectively. A mechanistic pathway for the reaction of acetylene is suggested to start with the formation of a weak $B(C_6F_5)_3$/acetylene adduct followed by a deprotonation of this species with any mentioned Lewis bases (LB) yielding the acetylide salts [LBH][$(C_6F_5)_3$B-C≡CH]. Alternatively nucleophilic addition of the LB to this adduct occurs to yield LBC(H)=C(H)B$(C_6F_5)_3$ compounds. Formation of **1** and **2b** is explained by the reactions of [LBH][$B(C_6F_5)_3$-C≡CH] salts with a second equivalent of $B(C_6F_5)_3$ to undergo electrophilic addition forming the vinylidene adduct $(C_6F_5)_3B^{-}$-C^{+}=C(H)B$(C_6F_5)_3$, which is subsequently stabilized by 1,2-migration of a C_6F_5 group to form [$(C_6F_5)_2$B-C(C_6F_5)=C(H)B$(C_6F_5)_3$]. The reaction between $B(C_6F_5)_3$ and phenylacetylene yielded a mixture of *Z*- and *E*-PhC(H)=C(C_6F_5)B$(C_6F_5)_2$ (**10-*Z*** and **10-*E***) confirming that the reaction proceeds via an acetylene/vinylidene rearrangement and subsequent 1,2 shift of a C_6F_5 group to the carbenic center. The FLPs **TMP**$\cdots B(C_6F_5)_3$ and *t*$Bu_3P\cdots B(C_6F_5)_3$ were converted with phenylacetylene or 3-ethynylthiophene to yield the acetylide products [**TMP**H][PhC≡CB$(C_6F_5)_3$] **4,** [**TMP**H][SC_4H_3C≡CB$(C_6F_5)_3$] **5**, [*t*-Bu_3PH][PhC≡CB$(C_6F_5)_3$] **6** and [*t*-Bu_3PH][SC_4H_3C≡CB$(C_6F_5)_3$] **7**, where **TMP** and *t*-Bu_3P acted as a base deprotonating the acetylenic proton. When FLP **Lut**$\cdots B(C_6F_5)_3$ was reacted with phenylacetylene or

3-ethynylthiophene, the deprotonated product [**LutH**][PhC≡CB(C_6F_5)$_3$] **8** (47 %) and the 1,2-addition compound **Lut**C(SC_4H_3C)=C(H)B(C_6F_5)$_3$ **9** (55 %) were obtained. Compounds **1-*E***, **2a-*E***, **4** and **5** were characterized by X-ray diffraction studies.

Introduction

The strong Lewis acid tris(pentafluorophenyl)boron is capable of strongly polarizing hydrogen and carbon centers of high and medium hardness shaping them for further reactivities. In the realm of the metallocene Ziegler-type polymerization catalysis metal carbon bonds were seen to be heterolytically cleaved by B(C_6F_5)$_3$ leaving vacant sites behind. In addition electrophilic carbon centers could be opened up by B(C_6F_5)$_3$ addition to coordinated or non-coordinated π systems.[1-5] Besides, Lewis acid B(C_6F_5)$_3$ were shown to be capable of inducing novel transformations,[6,7] or were employed as a stoichiometric reagents to generate new types of organometallic and organic compounds.[8-10] More recently, D. W. Stephan et al discovered that H_2 can reversibly be activated with heterolytic splitting by the "metal-free" internal Lewis pair [(2,4,6-$Me_3C_6H_2$)$_2$PC_6F_4B(C_6F_5)$_2$].[11] Based on this finding "metal-free" catalysts could developed for the hydrogenation of bulky imines with the Lewis acid B(C_6F_5)$_3$[12]. This type of reactivity required the formation of encounter complexes called frustrated Lewis pairs (FLPs) consisting of sterically hindered Lewis bases in combination with sterically hindered Lewis acids providing "unquenched" reactivity and prevention of Lewis pair formation. FLPs possess great potential in small molecule chemistry.[13-14] B(C_6F_5)$_3$, because of its strong Lewis acidity and its bulkiness, was demonstrated to be an appropriate constituent of FLPs and in combination with sterically hindered phosphines, amines and carbenes, it allowed facile cleavage of H_2.[15-23] Besides of this H_2 splitting capability ionic products were shown to serve as efficient catalysts for the hydrogenation of imines, nitriles and aziridines, as well as enamine and silyl enol C=C double bonds.[24-26] In addition, FLPs with B(C_6F_5)$_3$ can undergo 1,2-addition to olefins together with the Lewis base,[16,17] open the THF ring in a bifunctional manner,[19,27] activate B-H,[28] and N-H bonds,[18] but only little has been reported about the reaction of such FLPs towards

alkynes.[29,30] Stephan et al. have shown that FLPs can promote 1,2-addition reactions with substituted terminal alkynes to yield donor/acceptor substituted alkenes of type **A** or undergo C-H deprotonation to establish ionic products of type **B**.

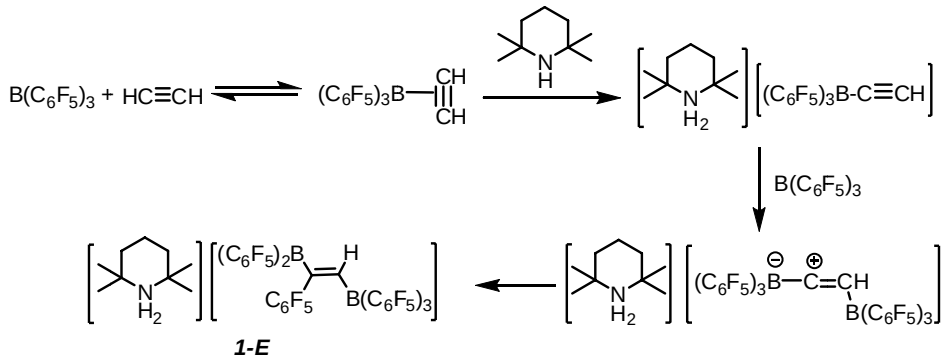


In this article we describe reactions between various FLPs and acetylene or substituted terminal alkynes.

Results and Discussion

Ia. Reactions of acetylene with FLPs of $B(C_6F_5)_3$ and TMP, *t*-Bu_3P and Lut

When dried HC≡CH was introduced into the toluene solution of FLP **TMP**···$B(C_6F_5)_3$, the reaction mixture turned orange and an oil separated at the bottom of Young NMR tube after 30 min. Hexane was added to the oily residue to prompt precipitation of the ionic compound $[(C_6F_5)_2B\text{-}C(C_6F_5)=C(H)\text{-}B(C_6F_5)_3]$[**TMP**H] **1-*E*** (Scheme 6.1), which was isolated as an off-white solid in 56 % yield. Multinuclear NMR in $CDCl_3$ showed that **1-*E*** exhibits a broad ^{1}H NMR resonance at 5.32 ppm attributable to the N*H* proton, as well as a resonance at 9.32 ppm assigned to the unique =C*H* proton. The ^{19}F NMR spectrum showed three sets of *o*-, *p*- and *m*- C_6F_5 signals. One set of resonance at δ -140.6, -159.2, -165.1 ppm was attributed to the carbon bound C_6F_5 unit, the other two sets of ^{19}F NMR resonances were detected at δ -132.1, -151.7, -162.8 ppm and at δ -131.7, -162.3, -167.1 ppm in agreement with C_6F_5 residues bound to three-coordinate ($\Delta\delta_{p,m}$ = 11.1) and four-coordinate boron centers ($\Delta\delta_{p,m}$ = 4.8).[31,32] In the ^{11}B NMR spectrum one signal at -15.2 ppm was assigned to the four-coordinate boron moiety, but no signal was observed for the three-coordinate boron center of the anion. The X-ray crystallographic study confirmed the spectroscopically derived *E*-vinylidene structure of the anion of **1-*E***1,2-connected to two different boron fragments $-B(C_6F_5)_3$ and $-B(C_6F_5)_2$ possessing a C=C distance of 1.363(3) Å. The electron deficient



Scheme 6.1

boron center is in a trigonal arrangement deviating somewhat from planarity, in which the three B-C bond distances (B2-C2 1.532(3), B2-C27 1.589(3), B2-C33 1.577(3) Å) are longer than those in the pseudo-tetrahedral geometry of the $B(C_6F_5)_3$ substituent (B1-C1 1.634(3), B1-C3 1.674(3), B1-C9 1.648(3), B1-C15 1.650(3) Å). A very important structural feature of **1-*E*** is the parallel arrangement of the unique C bound C_6F_5 group with one of the B-C_6F_5 groups, which is supposed to further stabilize the compound via π stacking of the aryl substituents. The ions are connected through multiple weak C-H···F hydrogen bonding contacts.

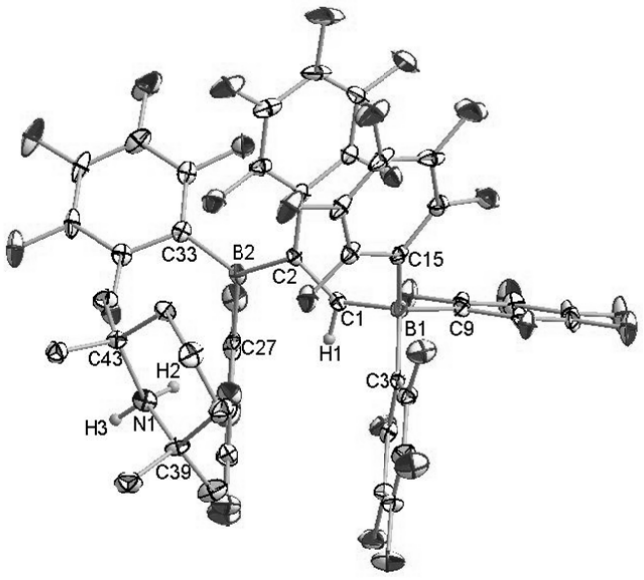
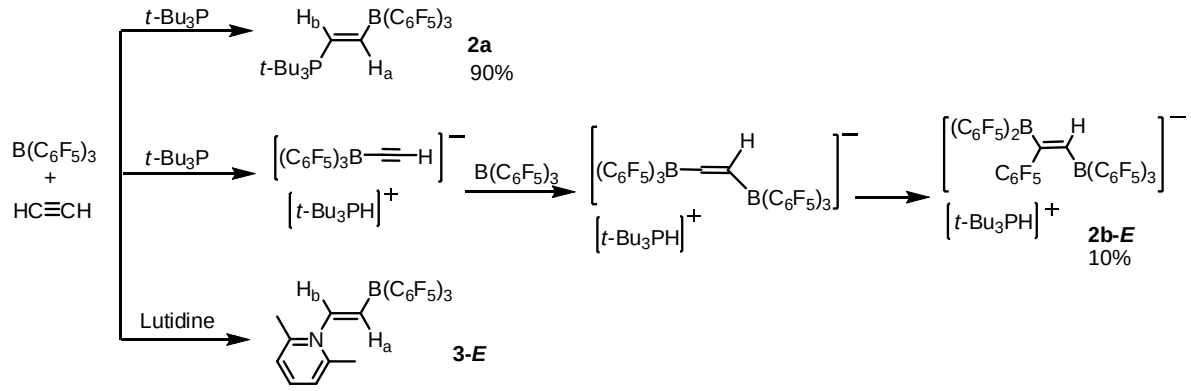


Figure 6.1 Molecular structure of ***1-E.*** *Hydrogen atoms except for the H_N and the H_{C1} are omitted for clarity.*

A possible reaction mechanism for the formation of **1-*E*** would start from the presumably weak terminal alkyne/$B(C_6F_5)_3$ adduct, which thus gets polarized with an increase in the acidity of the acetylenic hydrogens. In the presence of **TMP** the acidic C-H bond of the terminal alkyne was deprotonated to form the σ-acetylide adduct $[B(C_6F_5)_3\text{-}C{\equiv}CH]^-$. This anion behaves as a nucleophile at the *β*-position adding $B(C_6F_5)_3$ to afford the vinylidene adduct $(C_6F_5)_3B^-\text{-}C^+{=}C(H)B(C_6F_5)_3$. This zwitterionic species possesses a strongly electrophilic *α*-carbon center triggering similar to a Wolf rearrangement the 1,2-shift of a perfluorophenyl group to the more stable **1-*E*** product. This perfluorophenyl group migration could also be found in the reaction of $B(C_6F_5)_3$ with phenylacetylene (*vide infra* Scheme 6.6).

The related reactions of the FLPs *t*-$Bu_3P\cdots B(C_6F_5)_3$ and **Lut**$\cdots B(C_6F_5)_3$ with acetylene were also investigated. Similar to the reaction to **1-*E***, after dried HC≡CH was introduced into the toluene solution of *t*-$Bu_3P\cdots B(C_6F_5)_3$ FLP an oil separated at the bottom of Young NMR tube after 30 min. The isolated off-white product was characterized as a mixture containing about 90% of *E*-*t*-$Bu_3PC(H){=}C(H)B(C_6F_5)_3$ **2a-*E*** and about 10% of [*t*-Bu_3PH][*E*-$(C_6F_5)_2B\text{-}C(C_6F_5){=}C(H)B(C_6F_5)_3$] **2b-*E***. The ^1H and ^{31}P NMR of **2b** exhibit typical resonances for its cation and the ^{19}F and ^{11}B NMR spectra are similar to those resonances seen for $[B(C_6F_5)_2C(C_6F_5){=}C(H)B(C_6F_5)_3]^-$ anion of **1-*E***. In the ^1H NMR spectrum **2a-*E*** features two triplet resonances at 8.24 ppm (t, J = 21 Hz) and 5.60 ppm (t, J = 21 Hz) for H_a and H_b (Scheme 6.2). The triplet splitting pattern is anticipated to be caused by similar H-H and H-P coupling constants (Figure 6.2). The ^{31}P NMR signal for **2a-*E*** was found at 36.3 ppm and the ^{11}B NMR resonance at -14.3 ppm. The ^{19}F NMR spectrum of **2a-*E*** showed signals at δ -132.8 (*o*-), -162.3 (*p*-), -166.9 ppm (*m*-C_6F_5) originating from the four-coordinate boron atom. A single-crystal X-ray analysis confirms the formulation of **2a-*E*** as *E*-*t*-$Bu_3PC(H){=}C(H)B(C_6F_5)_3$ (Figure 6.3). The distances of C1-C2 (1.333(3) Å) and C1-B (1.612(3) Å) are quite comparable to those in **1-*E***. The C2-P bond length was found to be 1.787(2) Å, which is unexceptionally long.



Scheme 6.2

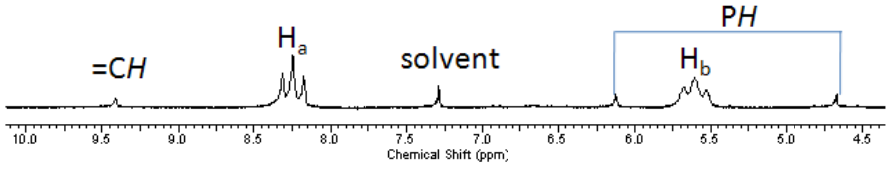


Figure 6.2 ^{1}H *NMR spectrum of the mixture of* ***2a-E*** *and* ***2b-E*** *in* $CDCl_3$.

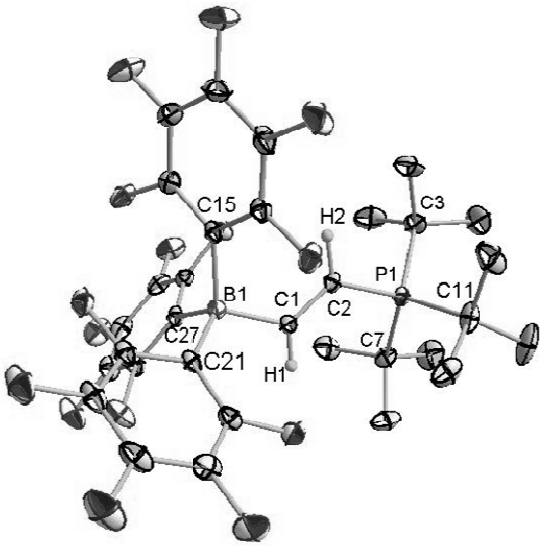


Figure 6.3 Molecular structure of ***2a-E.*** *Hydrogen atoms except for* H_{C1} *and* H_{C2} *are omitted for clarity.*

It should be pointed out that **TMP** and *t*-Bu_3P exhibit similar basicities (pK_a for *t*-Bu_3P is 11.4 and for **TMP** is 11.07)[33-35] so that the difference of the reaction paths of FLPs

TMP···$B(C_6F_5)_3$ and *t*-Bu_3P···$B(C_6F_5)_3$ with acetylene are thought to originate from the difference in sterics of these Lewis bases. Enhanced steric congestion leads preferentially to deprotonation; less steric hindrance provokes 1,2-addition to the acetylenic moiety. In the case of compounds **2** there is apparently competition between deprotonation and 1,2-addition. But *t*-Bu_3P may not big enough to prevent attacking one carbon atom of acetylene, so the majority is 1,2-addition product, only small amount of C_{sp}-H deprotonated product in the mixture.

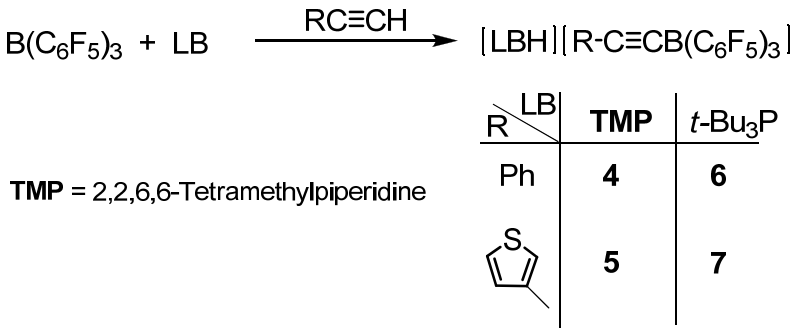
Selected bond lengths [Å] and Selected bond angles [°] of **1-*E*** and **2a-*E***

Compound 1-E					
C1-H1	0.958(17)	N1-H3	0.90(2)	N1-H2	0.93(2)
N1-C39	1.537(3)	N1-C43	1.540(3)	B1-C1	1.634(3)
B1-C3	1.674(3)	B1-C9	1.648(3)	B1-C15	1.650(3)
B2-C2	1.532(3)	B2-C27	1.589(3)	B2-C33	1.577(3)
C1-C2	1.363(3)	C39-N1-C43	121.27(15)	C39-N1-H2	107.7(14)
C43-N1-H2	103.5(13)	C39-N1-H3	110.2(13)	C43-N1-H3	107.6(14)
H2-N1-H3	105.2(18)	C1-B1-C9	109.92(15)	C1-B1-C15	108.24(16)
C9-B1-C15	114.67(16)	C1-B1-C3	106.86(15)	C9-B1-C3	104.96(15)
C15-B1-C3	111.91(15)	C2-B2-C33	127.65(17)	C2-B2-C27	119.33(17)
C33-B2-C27	113.00(16)				
Compound 2a-E					
C1-C2	1.333(3)	C1-B1	1.612(3)	C1-H1	0.90(2)
C2-P1	1.787(2)	C2-H2	1.01(3)	C3-P1	1.887(3)
C7-P1	1.888(2)	C11-P1	1.887(2)	C15-B1	1.659(3)
C21-B1	1.654(3)	C27-B1	1.656(3)	C2-P1-C11	105.77(10)
C2-P1-C3	104.61(11)	C11-P1-C3	112.35(13)	C2-P1-C7	109.97(11)
C11-P1-C7	112.23(11)	C3-P1-C7	111.45(12)	C1-B1-C21	113.90(17)
C1-B1-C27	100.92(16)	C21-B1-C27	112.81(17)	C1-B1-C15	110.86(17)
C21-B1-C15	105.02(16)	C27-B1-C15	113.61(17)		

The reaction of lutidine (**Lut**) and $B(C_6F_5)_3$ leads first of all to a classical Lewis acid-base adduct, which was however found to display FLP behavior in the activation of H_2.[23] In toluene solution an equilibrium is established observing in the ^1H NMR spectra at room temperature both the Lewis adduct and the free Lewis acid and base. Purging the reaction

mixture with acetylene at 80°C for 20 h, only the 1,2 addition product **Lut**C(H)=C(H)B(C_6F_5)$_3$ **3-*E*** could be isolated, which like **2a-*E*** could envisaged to be formed by nucleophilic addition of **Lut** to a weak σ or π B(C_6F_5)$_3$/acetylene adduct (Scheme 6.2). **3-*E*** was isolated in 34 % yield. **3-*E*** features ^{1}H NMR resonances at 6.66 (d, J = 15Hz) and 6.18 (d, J = 15Hz) for H_a and H_b (Scheme 6.2). The ^{19}F NMR signals are located at δ -133.1 (*o*-), -163.8 (*p*-), -168.0 ppm (*m*-C_6F_5) and are quite similar to those found for compound **3-*E***. This observation would support the view that the less sterically hindered Lewis bases favor the formation of 1,2-additon products in the reactions of their FLPs with acetylene.

The reaction of phenylacetylene (PhC≡CH) or 3-ethylthiophene (SC_4H_3C≡CH) with the **TMP**···B(C_6F_5)$_3$ or *t*-Bu_3P···B(C_6F_5)$_3$ FLPs proceeded exclusively along the deprotonation pathway forming the respective salts [**TMP**H][PhC≡CB(C_6F_5)$_3$] **4,** [**TMP**H][SC_4H_3C≡CB(C_6F_5)$_3$] **5**, [*t*-Bu_3PH][PhC≡CB(C_6F_5)$_3$] **6** and [*t*-Bu_3PH][SC_4H_3C≡CB(C_6F_5)$_3$] **7** (Scheme 6.3).



Scheme 6.3

In the ^{1}H NMR spectra of **4** and **5** broad H_N resonances appear at δ 4.04 and 4.13 ppm witnessing the presence of ammonium cations. The ^{19}F and ^{11}B NMR spectra are quite similar for **4** (^{19}F NMR: δ -133.9, -164.1, -168.2 ppm; ^{11}B NMR: δ -18.6 ppm) and **5** (^{19}F NMR: δ -133.9, -164.2, -168.2; ^{11}B NMR: δ -18.5 ppm) pointing to structural similarities of these compounds. Compound **6** and **7** exhibit the same ^{19}F and ^{11}B NMR resonances as those in **4** and **5**. And the cation of **6** and **7** show the typical resonance in ^{1}H and ^{31}P NMR spectrum. The X-ray structural analysis of **4** shows that the boron atom adopts a pseudo-tetrahedral

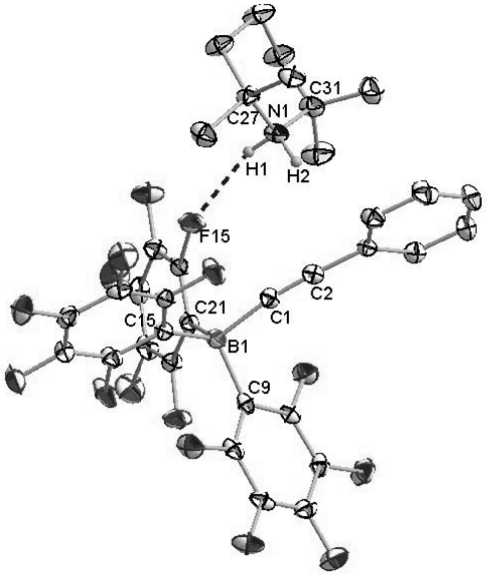


Figure 6.4 Molecular structure of ***4.*** *Hydrogen atoms except for the H_N atom are omitted for clarity.*

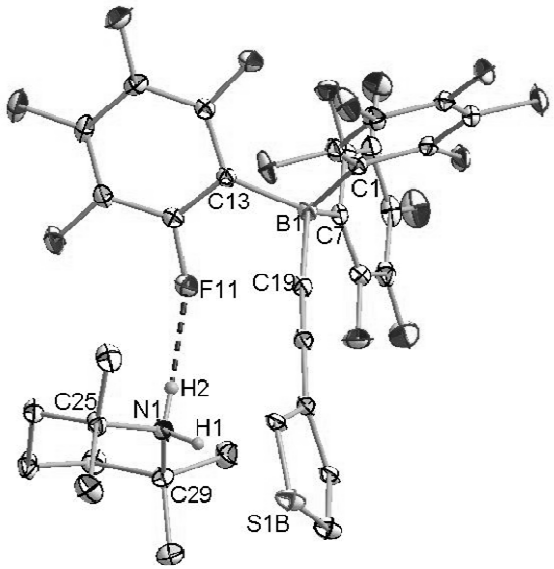


Figure 6.5 Molecular structure of ***5.*** *Hydrogen atoms except for the H_N atom are omitted for clarity.*

geometry with a B-C(*sp*) bond distance of 1.5934(19) Å, much shorter than the other three B-C(sp^2) bond distances (B1-C9,1.653(2); B1-C15 1.644(2); B1-C21 1.6676(19) Å) (Figure

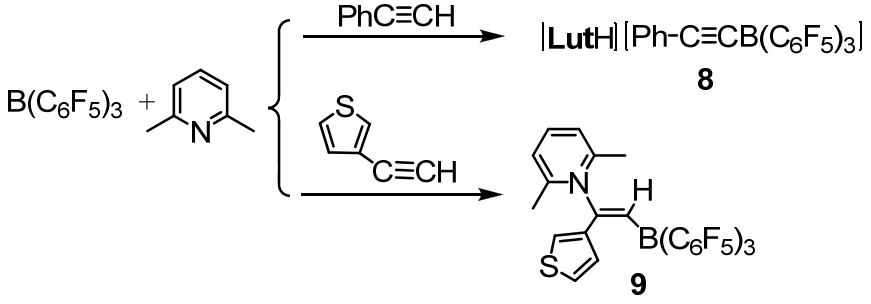
6.4). The ions are connected through a weak N-H···F hydrogen bond, the separation between H1 and F15 is 2.21 Å. A crystallographic study of **5** (Figure 6.5) revealed a structure related to **4** with the counterions also connected through weak N-H···F hydrogen bonding of H1-F11 at a distance of 2.22 Å. The B-C(*sp*) and N-H bond lengths of 1.5969 (17) Å and 0.864 Å are comparable to those in **4**.

Selected bond lengths [Å] and Selected bond angles [°] of **4** and **5**

Compound 4					
N1-H1	0.881(16)	N1-H2	0.914(17)	N1-C27	1.5387(17)
N1-C31	1.5371(18)	B1-C9	1.653(2)	B1-C15	1.644(2)
B1-C21	1.6676(19)	B1-C1	1.5934(19)	H1-N1-H2	103.5(14)
H1-N1-C27	105.6(10)	H1-N1-C31	106.1(10)	H2-N1-C27	108.5(10)
H2-N1-C31	110.2(10)	C31-N1-C27	121.37(10)	C1-B-Cl5	112.78(10)
C1-B1-C9	102.93(11)	C15-B1-C9	114.36(11)	C1-B1-C21	109.37(11)
C15-B1-C21	106.67(10)	C9-B1-C21	110.71(10)		
Compound 5					
N1-H1	0.874(16)	N1-H2	0.852(17)	N1-C25	1.5398(16)
N1-C29	1.5394(15)	B1-C1	1.6479(18)	B1-C7	1.6440(18)
B1-C13	1.6609(17)	B1-C19	1.5969(17)	H1-N1-H2	108.9(14)
H1-N1-C29	108.1(9)	H1-N1-C25	107.2(10)	H2-N1-C29	107.0(11)
H2-N1-C25	104.4(11)	C29-N1-C25	120.84(9)	C1-B1-C7	112.76(9)
C1-B1-C13	113.41(9)	C19-B1-C7	113.22(10)	C1-B1-C19	102.86(9)
C19-B1-C13	109.23(9)	C7-B1-C13	105.53(9)		

We suppose that at higher temperatures the **Lut**-$B(C_6F_5)_3$ adduct dissociates with formation of a **Lut**···$B(C_6F_5)_3$ FLP in concentrations sufficient for subsequent reactivity. Indeed, phenylacetylene (PhC≡CH) and 3-ethylthiophene (SC_4H_3C≡CH) were sought to be transformed in the presence of **Lut** and $B(C_6F_5)_3$. We reckoned that the lower basicity of **Lut** in comparison with **TMP** or *t*-Bu_3P would cause the deprotonation pathway to be less preferred and that **Lut** would mainly react as a Lewis base. The reaction between PhC≡CH and SC_4H_3C≡CH proceeded sluggishly producing [**LutH**][PhC≡$CB(C_6F_5)_3$] **8** (47 %) and **Lut**$C(SC_4H_3C)$=C(H)$B(C_6F_5)_3$ **9** (55 %) (Scheme 6.4). The ^{1}H NMR spectrum of **8** showed a

broad signal attributable to the H_N nucleus at 12.30 ppm. The ^{19}F and ^{11}B NMR spectrum of **8** were found to be quite similar to those of **4** or **5**. The ^{1}H NMR signal for the vinyl proton of **9** is located at 6.74 ppm. One set of ^{19}F NMR signals for the aryl substituents (δ -132.8, -163.7, -168.1 ppm) and one ^{11}B NMR signal (δ -16.4 ppm) are in agreement with a four-coordinate boron.

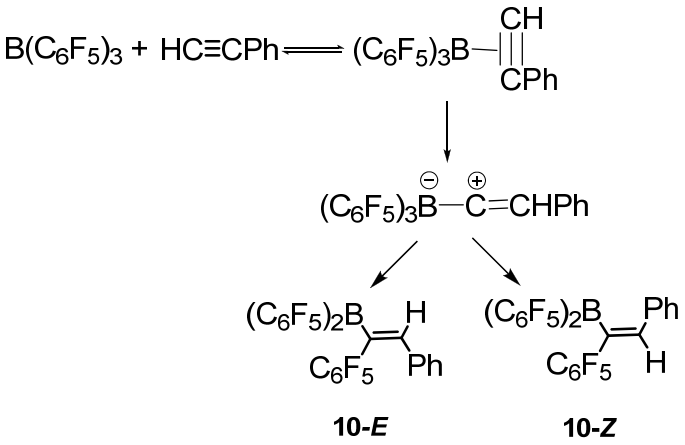


Scheme 6.4

Ib. Reactions of phenylacetylene (PhC≡CH) and 3-ethylthiophene (SC_4H_3C≡CH) with $B(C_6F_5)_3$

Further studies were carried out in the absence of a Lewis base, which caused another reaction pathway to become prevalent. A 1:1 mixture of $B(C_6F_5)_3$ and PhC≡CH turned in toluene solution deep red and according to ^{1}H and ^{19}F NMR spectrum two products were identified as the isomers *Z*- and *E*-PhC(H)=C(C_6F_5)B(C_6F_5)$_2$ **10-*Z*** and **10-*E*** (Scheme 6.5). The ^{1}H NMR spectra exhibited resonances at 7.73 and 7.59 ppm, respectively. The ^{19}F NMR spectra revealed several sets of signals attributable to both a carbon bound -C_6F_5 unit (**10-*E***: -144.4, -156.2, -162.6 ppm; **10-*Z***:-140.8, -156.6, -162.6 ppm) and two boron bound -C_6F_5 units (**10-*E***: -130.6, -147.4, -163.8 ppm; **10-*Z***: -131.9, -148.5, -163.8 ppm).[35] It is reasonable to assume that an acetylene/vinylidene rearrangement had taken place and that related to a Wolff rearrangement[36,37] the highly electrophilic α-carbon center of the formed vinylidene intermediate [$(C_6F_5)_3B^-$-C^+=C(H)Ph] became saturated by a boron to carbon C_6F_5-1,2-shift. The reaction between $B(C_6F_5)_3$ and PhC≡CH was very fast, which made it impossible to trace

intermediates.[38,39] Furthermore the ***Z***- and ***E***-isomers of $PhC(H)=C(C_6F_5)B(C_6F_5)_2$ were found to be inert toward bulky Lewis bases so that products other than **10**-***E*** and **10**-***Z*** could not be found.



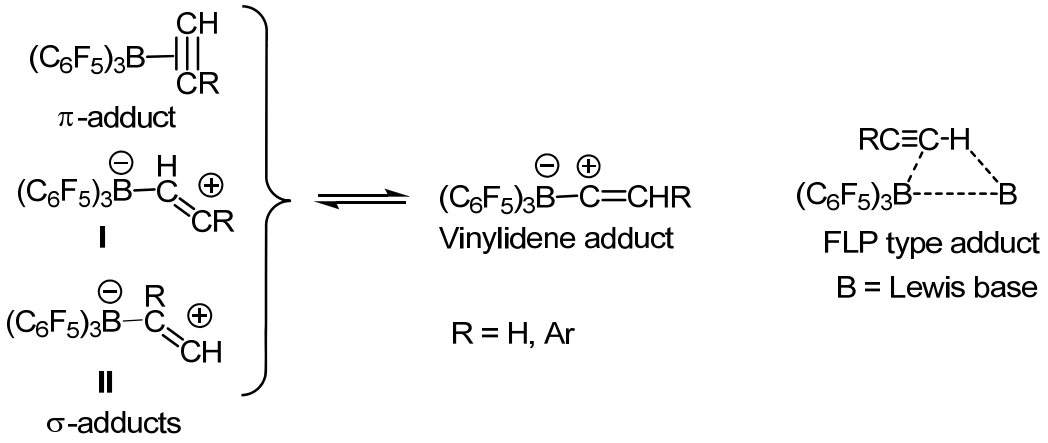
Scheme 6.5

Unlike the reaction between $B(C_6F_5)_3$ and PhC≡CH, the reaction of a 1:1 mixture of SC_4H_3-C≡CH and $B(C_6F_5)_3$ could not be driven to completeness and most of the $B(C_6F_5)_3$ Lewis acid remained unreacted even after prolonged reaction times at room temperatures. Only a trace amount of SC_4H_3-$CH=C^+$-$B^-(C_6F_5)_3$ was formed exhibiting a set of ^{19}F NMR signals at δ -129.8, -160.7, -165.7 ppm. Based on a signal at 8.1 ppm in the ^1H NMR spectrum a S···*H* hydrogen bonding contact seemed to be present. Presumably the $S_{thiophene}$ atom acts as a Lewis base and prevents proper contact between the acetylenic π-bond of the SC_4H_3-C≡CH molecule. The very low concentration of this complex seemed however sufficient for a deprotonation with strong Lewis base or for 1,2-addition with weak Lewis base so that compound **5**, **7**, **9** could be formed.

Ic. DFT calculations

It became evident from Schemes 1 - 5 that the activation of acetylenes by $B(C_6F_5)_3$ could be envisaged by primary weak interactions of both reaction partners, which could be established in form of a σ or a π complex (Scheme 6.6). In the additional presence of a base (Lewis base)

we could envisage stepwise activation with initial formation of the σ or π adducts and their subsequent deprotonation. Alternatively bifunctional activation through a four-centered FLP type arrangement could occur transferring the acetylide unit to the Lewis acid $B(C_6F_5)_3$ and the proton to the base (Lewis base) in a more or less concerted fashion (Scheme 6.6).



Scheme 6.6

The acetylene/vinlyidene rearrangement is anticipated to be base mediated proceeding with a deprotonation/protonation sequence or could simply operate on the basis of a proton shift preferably via a σ adduct.

The calculations revealed no stabilized form of interaction with acetylene of the kinds sketched in Scheme 6.6, since no prominent local minima were found on the energy hypersurface during the optimization process. This might be due to deficiencies to the DFT calculational procedures not representing well polar structures with considerable charge separation of the σ or π type. For the interaction of $B(C_6F_5)_3$ with phenyl acetylene, however, a local minimum could be localized for the σ adduct **I** (Figure 6.6). The formation of this σ-type adduct is slightly endothermic (7.1 kcal/mol) with respect to the starting materials. Its potential energy would still be in a range to be easily reached by thermal activation. The isomeric σ adduct **II** was calculated to be unstable and it was not possible to find a local minimum for it.

The DFT optimization processes to establish vinylidene adducts did in both cases of R = H

and Ph not converge to a definite local minimum structure, but still we have to assume its transient existence, since it would ascribe the only topological alternative to eventually reach **10-*E*** and **10-*Z*** with consecutive 1,2-C_6F_5-shift. **10-*E*** and **10-*Z*** were calculated to possess high thermodynamic driving forces in their formations (-42.5 *vs.* -41.1 kcal/mol, respectively) with respect to the energetic level of free $B(C_6F_5)_3$ and acetylene. The slight energetic preference for **10-*E*** agree with the observation that this isomer is prevailing under experimental circumstances.

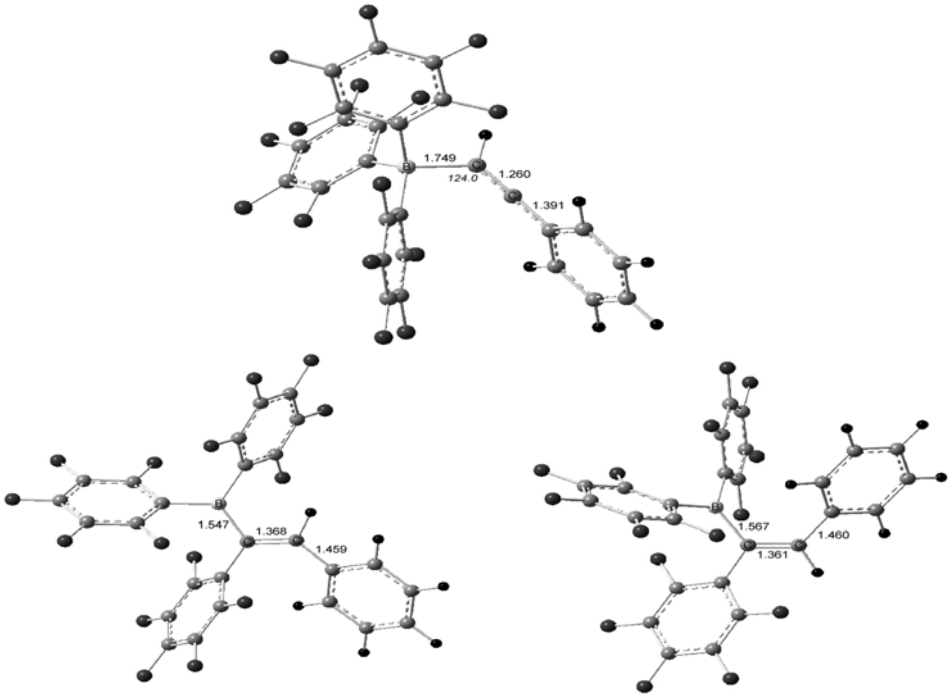


Figure 6.6 Optimized geometries and selected bond distances (Å) and angles (°) of ***10-E*** *(left),* ***10-Z*** *(right) and a possible σ-type intermediate (top) during the reaction of* $B(C_6F_5)_3$ *with phenylacetylene, calculated at the B3PW91/6-31+g(d) level.*

Conclusion

In summary, we have applied frustrated Lewis pairs LB···LA (**TMP**···$B(C_6F_5)_3$ *t*-Bu_3P···$B(C_6F_5)_3$ and **Lut**-$B(C_6F_5)_3$) for the activation of terminal alkynes, which furnished two different initial pathways:

a) deprotonation pathway

b) 1,2-addition pathway

The deprotonation pathway a) proceeded with deprotonation of any of the initial $(C_6F_5)_3B(\sigma\text{-},\pi\text{-}HC{\equiv}CR)$ complexes with the Lewis base acting as a base or with "bifunctional" heterolysis of the ≡C-H bond (Scheme 6.6). This bifunctional heterolysis would involve a four-centered transition state of the ≡C-H bond and the FLP encounter complex. For any of these mechanistic alternatives the primary products are the $[B(C_6F_5)_3\text{-}C{\equiv}CR][LBH]$ ion pairs (R = H, Ar). However, neither the experimental nor the theoretical studies did provide definite clues on the type of intermediate appearing in the reactions of Schemes 6.1-6.5.

Along pathway b) the Lewis pairs could be envisaged to undergo 1,2-additions to the alkynes to generate $LBC(R)=C(H)B(C_6F_5)_3$ structures. Initially, we anticipate for this case again primary interaction of the Lewis acid $B(C_6F_5)_3$ with the acetylenes via σ and π complexes (Scheme 6.6). The final step of nucleophilic addition of the LB should naturally depend on the nucleophilic character of the base as seen for *t*-Bu_3P and **LUT**. The regioselectivity of **LUT** addition to the higher substituted end of the $B(C_6F_5)_3$ adduct with $SC_4H_3C{\equiv}CH$ points to the involvement of the σ complex of type **I** or of the π complex (Scheme 6.6).

Boron to carbon C_6F_5-1,2-migrations were also seen to be an important feature of this chemistry. They appeared as follow-up reactions of initially formed $[B(C_6F_5)_3\text{-}C{\equiv}CH]^-$ anions of **1-*E*** and **2b-*E***, which then underwent $B(C_6F_5)_3$ addition. Subsequently this anion was transformed via C_6F_5 migration to an *E*-$[(C_6F_5)_2B\text{-}C(C_6F_5)=C(H)\text{-}B(C_6F_5)_3]^-$ product. The reaction of phenylacetylene with $B(C_6F_5)_3$ could be viewed a related 1,2 carboboration case[38] where the electrophilic carbon of the initially formed $(C_6F_5)_3B^-\text{-}C^+=C(H)R$ vinylidene species became saturated by the same migrational step to yield *E*- and *Z*-$RC(H)=C(C_6F_5)B(C_6F_5)_2$ compounds.[43]

Experimental part

General consideration: All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with

dry nitrogen. Solvents were freshly distilled under N_2 employing standard procedures and were degassed by freeze-thaw cycles prior to use. $B(C_6F_5)_3$ were synthesized according to the literature.[40] All other organic reagents were purchased from Aldrich and used without further purification. ^1H NMR, ^{19}F NMR, $^{31}P\{^1H\}$ NMR and $^{11}B\{^1H\}$ NMR data were recorded on a Varian Gemini-200 and 300 spectrometer. Chemical shift are expressed in parts per million (ppm) referenced to deuterated solvent used. ^{19}F, ^{11}B and ^{31}P NMR were referenced to $CFCl_3$, $BF_3{\cdot}OEt_2$ and 85 % H_3PO_4, respectively. Microanalyses were carried out at Anorganisch-Chemisches Institut of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoKα radiation, λ = 0.71073 Å).[41] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction[42] and data reduction were performed with the Oxford program suite *CrysAlisPro*.[43] The structures were solved with the direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[44] All programs used during the crystal structure determination process are included in the WINGX software.[45] The program PLATON[46] was used to check the results of the X-ray studies and to analyze the hydrogen-bonding systems.

Calculations were carried out at the DFT level of theory with the Gaussian03 program package[47] using the hybrid functional B3PW91[48,49] and the standard Pople 6-31G+(d) basis set.[50] Geometry optimizations were carried out without any symmetry restrictions, and the nature of the optimized minima was evaluated by computations of harmonic vibrational frequencies at the same theory level. The relative energies were calculated by correcting the B3LYP/6-31+G(d) total energies for zero-point vibrational energies (ZPE).

Preparation of [TMPH][$(C_6F_5)_2$B-C(C_6F_5)=C(H)-B($C_6F_5)_3$] 1-*E*

In a Young NMR tube, $B(C_6F_5)_3$ (0.0768 g, 0.15 mmol), 2,2,6,6-tetramethyl-piperidine (**TMP**) (0.0212 g, 0.15 mmol) were dissolved in 1 mL of toluene. Dried HC≡CH (1000 mbar,

ca. 0.15 mmol) was then filled into the NMR tube and shaken. The brown oil stuff formed at the bottom of the NMR tube 30 min later at room temperature. Then add hexane to the oil stuff to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as off-white solid. Yield: 56%. Crystals were obtained from a mixture of benzene/hexane at 25 °C. Anal. Calcd for $C_{47}H_{21}B_2F_{30}N$: C, 47.39; H, 1.78; N, 1.18. Found: C, 47.20; H,1.53; N, 1.43. ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.49 (s, 12H, -CH_3), 1.82 (m, 4H, CH_2), 1.89 (m, 2H, CH_2), 5.32 (br, 2H, NH_2), 9.36 ppm (s, 1H, C-*H*) ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz, 293 K): δ -15.2 ppm (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 293 K): δ -131.7 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -132.1 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -140.6 (d, 2F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -151.7 (t, 2F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -159.2 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -162.3 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -162.8 (t, 4F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5), -165.1 (t, 2F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5), -167.1 ppm (t, 6F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). The solubility of **1** was too low to permit C_6F_5 resonances of low intensity to be observed in the ^{13}C NMR spectrum.

X-ray Crystal Structure Analysis of **1-*E***: formula $C_{50}H_{24}B_2F_{30}N$, *M*r = 1230.32, Triclinic, *P*$\bar{1}$, *a* = 11.7619(4), *b* = 11.9617(4), *c* = 20.1408(7) Å, α = 84.658(3), β = 75.635(3), γ = 60.642(4)°, *V* = 2391.16(17) Å^3, *Z* = 2, D_c = 1.709 g cm^{-1}, μ = 0.181 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 30688 reflections collected, 9745 independent [$R_{(int)}$ = 0.0567] and 5597 observed reflections [$I > 2\sigma(I)$], 749 refined parameters, *R* = 0.0410, *w*R_2 = 0.08919. CCDC 748013.

Preparation of t-Bu_3PC(H)=C(H)B(C_6F_5)$_3$ 2a and [*t*-Bu_3PH][(C_6F_5)$_2$B-C(C_6F_5)=C(H)-B(C_6F_5)$_3$] 2b

In a Young NMR tube, B(C_6F_5)$_3$ (0.0768 g, 0.15 mmol), tri-*tert*-butylphosphine (0.03 g, 0.15 mmol) were dissolved in 1 mL of toluene. Dried HC≡CH (1000 mbar, *ca*. 0.15 mmol) was then filled into the NMR tube and shaken. The brown oil stuff formed at the bottom of the NMR tube 30 min later at room temperature. Then add hexane to the oil stuff to induce precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as off-white solid which contain about 90% of **2a** and 10% of **2b**. Yield: 56%. Crystals of **2a** were obtained from a mixture of toluene/hexane at 25 °C. **2a**: ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.55 (d, 27H, $^3J_{H\text{-}P}$ = 12 Hz, P{C(CH_3)$_3$}$_3$), 5.60 (t, overlap, *J* = 21 Hz,

=C-*H*), 8.24 ppm (t, overlap, J = 21 Hz, =C-*H*).^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz, 293 K): δ -14.3 ppm (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 293 K): δ 36.3 ppm (s). ^{19}F NMR ($CDCl_3$, 282 MHz, 293 K): δ -132.8 (d, 6F, $^{3}J_{FF}$ = 23 Hz, *o*-C_6F_5), -162.3 (t, 3F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -166.9 ppm (t, 6F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 282 MHz, 293 K): δ 147.9 (dm, $^{1}J_{C\text{-}F}$ = 238 Hz, *o*-C_6F_5), 138.6 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *p*-C_6F_5), 136.5 (dm, $^{1}J_{C\text{-}F}$ = 238 Hz, *m*-C_6F_5), 101.9, 101.1 (=*C*H), 39.6 (d, $^{1}J_{C\text{-}P}$ = 32 Hz, P{*C*$(CH_3)_3$}$_3$), 30.0 ppm (s, P{C(*C*H_3)$_3$}$_3$). **2b**: ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 1.67 (d, 27H, $^{3}J_{H\text{-}P}$ = 15 Hz, P{C$(CH_3)_3$}$_3$), 5.4 (d, 1H, $^{1}J_{H\text{-}P}$ = 440 Hz, P-*H*), 9.41 ppm (s, 1H, =C-*H*). ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz, 293 K): δ -15.1 ppm (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 293K): δ 58.1 ppm (s).

X-ray Crystal Structure Analysis of **2a-*E***: formula $C_{39}H_{37}BF_{15}P$, *M*r = 832.47, Monoclinic, $P2_1/c$, a = 12.3469(2), b = 18.0538(2), c = 17.8463(2) Å, β = 104.935(2)°, V = 3843.71(9) Å^3, Z = 4, D_c = 1.439 g cm^{-1}, μ = 0.173 mm^{-1}, λ = 0.71073 Å, T = 183(2) K, 33277 reflections collected, 7864 independent [$R_{(int)}$ = 0.026] and 5618 observed reflections [$I > 2\sigma(I)$], 523 refined parameters, R = 0.050, wR_2 = 0.134. CCDC 748014.

Preparation of LutC(H)=C(H)B(C_6F_5)$_3$ 3

In a Young NMR tube, B(C_6F_5)$_3$ (0.0768 g, 0.15 mmol), Lutidine (**Lut**) (0.016 g, 0.15 mmol) were dissolved in 1 mL of toluene. Dried HC≡CH (1000 mbar, *ca*. 0.15 mmol) was filled into the NMR tube and kept the NMR tube at 80 °C for 20 h. Hexane was then add to the mixture solution to induce precipitation. The mixture was filtered, washed with hexane and ethyl ether and dried *in vacuo*. The product was collected as white solid. Yield: 34%. Anal. Calcd for $C_{27}H_{11}BF_{15}N$: C, 50.26; H, 1.72; N, 2.17. Found: C, 50.17; H,1.68; N, 2.19. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 2.52 (s, 6H, -CH_3), 6.18 (d, 1H, $^{3}J_{H\text{-}H}$ = 18 Hz, =C*H*), 6.66 (d, 1H, $^{3}J_{H\text{-}H}$ = 18 Hz, =C*H*), 7.62 (d, 2H, $^{3}J_{H\text{-}H}$ = 6 Hz, *m*-C_5H_3N), 8.10 ppm (t, 1H, $^{3}J_{H\text{-}H}$ = 6 Hz, *p*-C_5H_3N). ^{11}B{^{1}H} NMR (CD_3CN, 96 MHz, 293 K): δ -15.9 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ -133.1 (d, 6F, $^{3}J_{FF}$ = 23 Hz, *o*-C_6F_5), -163.8 (t, 3F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -168.0 ppm (t, 2F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz, 293 K) (partial): 157.2, 144.9, 127.2, 21.9 ppm.

Preparation of [TMPH][PhC≡CB(C_6F_5)$_3$] 4

$B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), 2,2,6,6-tetramethyl-piperidine (**TMP**) (0.0283 g, 0.2 mmol), phenylacetylene (0.021 g, 0.2 mmol) were dissolved in 2 mL of toluene and allowed the orange solution to stir at room temperature for 30 min. The reaction mixture was then concentrated to half of its original volume and hexane (5 mL) was added to promote precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as white solid. Yield: 87％. Crystals were obtained from a mixture of toluene/hexane at 25 °C. Anal. Calcd for $C_{35}H_{25}BF_{15}N$: C, 55.65; H, 3.34; N, 1.85. Found: C, 55.54; H,3.41; N, 1.83. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 0.41 (s, 12H, -CH_3), 0.55 (m, 4H, CH_2), 0.59 (m, 2H, CH_2), 4.04 (br, 2H, NH_2), 6.80 (d, 2H, $^3J_{HH}$ = 1.8Hz, Ph-*H*), 6.82 (d, 1H, $^3J_{HH}$ = 2.1Hz, Ph-*H*), 7.14 ppm (m, 2H, Ph-*H*). ^{11}B{^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ -18.6 ppm (s). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ -133.9 (d, 6F, $^3J_{FF}$ = 25 Hz, *o*-C_6F_5), -164.1 (t, 3F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -168.2 ppm (t, 6F, $^3J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 149.5 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5), 139.7 (dm, $^1J_{C\text{-}F}$ = 227 Hz, *p*-C_6F_5), 137.7 (dm, $^1J_{C\text{-}F}$ = 256 Hz, *m*-C_6F_5), 132.7 (*o*-Ph), 132.3 (*p*-Ph), 127.4 (*m*-Ph), 84.0 (Ph-*C*CB), 77.7 (Ph-C*C*B), 54.2 (*o*-C_5H_7N), 36.5 (*m*-C_5H_7N), 29.5 (CH_3), 16.9 ppm (*p*-C_5H_7N).

X-ray Crystal Structure Analysis of **4**: formula $C_{35}H_{25}BF_{15}N$, *M*r = 755.37, Triclinic, *P*$\bar{1}$, *a* = 10.2056(11), *b* = 12.2576(8), *c* = 14.6323(8) Å, α = 70.676(3), β = 87.904(3), γ = 68.808(4)°, *V* = 1603.3(2) Å^3, *Z* = 2, D_c = 1.565 g cm^{-1}, μ = 0.152 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 20184 reflections collected, 7943 independent [$R_{(int)}$ = 0.0320] and 5663 observed reflections [$I > 2\sigma(I)$], 481 refined parameters, *R* = 0.0388, *w*R_2 = 0.0904. CCDC 748015.

Preparation of [TMPH][C_4H_3SC≡CB(C_6F_5)$_3$] 5

$B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), 2,2,6,6-tetramethyl-piperidine (**TMP**) (0.0283 g, 0.2 mmol), 3-Ethynylthiophene (0.022 g, 0.2 mmol) were dissolved in 2 mL of toluene forming a deep red solution and allowed to stir at room temperature for 30 min. The reaction mixture was then concentrated to half of its original volume and hexane (5 mL) was added to prompt precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product

was collected as light-brown. Yield: 86%. Crystals were obtained from a mixture of toluene/hexane at 25 °C. Anal. Calcd for $C_{33}H_{23}BF_{15}NS$: C, 52.06; H, 3.04; N, 1.84. Found: C, 52.21; H,3.08; N, 1.82. ^{1}H NMR (toluene-d_8, 300 MHz, 293 K): δ 0.47 (s, 12H, CH_3), 0.64 (m, 4H, -CH_2), 0.71 (m, 2H, CH_2), 4.13 (br, 2H, NH_2), 6.60 (m, 1H, C_4H_3S), 6.66 (m, 1H, C_4H_3S), 6.69 ppm (dd, 1H, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 2 Hz, C_4H_3S). ^{11}B{^{1}H} NMR (toluene-d_8, 96 MHz, 293 K): δ -18.5 ppm (s). ^{19}F NMR (toluene-d_8, 282 MHz, 293 K): δ -133.9 (d, 6F, $^{3}J_{FF}$ = 25 Hz, *o*-C_6F_5), -164.2 (t, 3F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -168.2 ppm (t, 6F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (toluene-d_8, 75 MHz, 293 K): δ 149.5 (dm, $^{1}J_{C\text{-}F}$ = 238 Hz, *o*-C_6F_5), 139.8 (dm, $^{1}J_{C\text{-}F}$ = 230 Hz, *p*-C_6F_5), 137.7 (dm, $^{1}J_{C\text{-}F}$ = 245 Hz, *m*-C_6F_5), 131.1 (C_4H_3S), 130.4 (C_4H_3S), 126.3 (C_4H_3S), 77.4 (*CC*B), 53.9 (*o*-C_5H_7N), 36.5 (*m*-C_5H_7N), 29.5 (*C*H_3), 16.9 (*p*-C_5H_7N).

X-ray Crystal Structure Analysis of **5**: formula $C_{33}H_{23}BF_{15}NS$, *M*r = 761.40, Triclinic, *P*$\bar{1}$, *a* = 11.0873(2), *b* = 12.1753(2), *c* = 12.7089(2) Å, α = 100.776(2), β = 101.541(2), γ = 103.953(2)°, *V* = 1580.61(5) Å^3, *Z* = 2, D_c = 1.600 g cm^{-1}, μ = 0.218 mm^{-1}, λ = 0.71073 Å, *T* = 183(2) K, 39687 reflections collected, 9654 independent [$R_{(int)}$ = 0.0241] and 7111 observed reflections [$I > 2\sigma(I)$], 473 refined parameters, *R* = 0.0401, *w*R_2 = 0.1114. CCDC 748016.

Preparation of [*t*-Bu_3PH][$C_4H_3SC{\equiv}CB(C_6F_5)_3$] 7

$B(C_6F_5)_3$ (0.1024 g, 0.2 mmol), tri-*tert*-butylphosphine (0.0405 g, 0.2 mmol), 3-Ethynylthiophene (0.022 g, 0.2 mmol) were dissolved in 2 mL of toluene forming a brown solution and allowed to stir at room temperature for 30 min. The reaction mixture was then concentrated to half of its original volume and hexane (5 mL) was added to prompt precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as light-brown solid. Yield: 82%. Anal. Calcd for $C_{36}H_{31}BF_{15}PS$: C, 52.57; H, 3.80. Found: C, 52.32; H, 3.72. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 1.6 (d, 27H, $^{3}J_{H\text{-}P}$ = 15 Hz, P{$C(CH_3)_3$}$_3$), 5.36 (d, 1H, $^{1}J_{H\text{-}P}$ = 444 Hz, P*H*), 1H, C_4H_3S), 6.90 (dd, 1H, *J* = 6 Hz, 2 Hz, C_4H_3S), 7.25 (d, 1H, *J* = 6 Hz, C_4H_3S), 7.28 (d, 1H, *J* = 6 Hz, C_4H_3S). ^{11}B{^{1}H} NMR (CD_3CN, 96 MHz, 293 K): δ -21.1 ppm (s). ^{31}P{^{1}H} NMR (CD_3CN, 121 MHz, 293 K): δ 57.0 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ -133.9 (d, 6F, $^{3}J_{FF}$ = 23 Hz, *o*-C_6F_5), -164.5 (t, 3F, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -168.6 ppm (t, 6F, $^{3}J_{FF}$ = 20 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR

(CD_3CN, 75 MHz, 293 K) (partial): δ 149.0 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5), 139.5 (dm, $^1J_{C\text{-}F}$ = 230 Hz, *p*-C_6F_5), 137.8 (dm, $^1J_{C\text{-}F}$ = 242 Hz, *m*-C_6F_5), 130.8 (C_4H_3S), 130.6 (C_4H_3S), 125.9 (C_4H_3S), 38.2 (d, $^1J_{C\text{-}P}$ = 28 Hz, P{*C*(CH_3)$_3$}$_3$), 30.1 ppm (s, P{C(*C*H_3)$_3$}$_3$).

Preparation of [LutH][PhC≡CB(C_6F_5)$_3$] 8

B(C_6F_5)$_3$ (0.1024 g, 0.2 mmol), Lutidine (**Lut**) (0.021 g, 0.2 mmol), phenylacetylene (0.021 g, 0.2 mmol) were dissolved in 2 mL of toluene and allowed the yellow solution to stir at 80^{o}C for 8 h. The reaction mixture was then concentrated to half of its original volume and hexane (5 mL) was added to promote precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as yellow solid. Yield: 37%. Anal. Calcd for $C_{33}H_{15}BF_{15}N$: C, 54.95; H, 2.10; N, 1.94. Found: C, 54.71; H, 2.08; N, 1.82. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 2.58 (s, 6H, -CH_3), 7.22 (m, 5H, Ph-*H*), 7.44 (d, 2H, $^3J_{H\text{-}H}$ = 6 Hz, *m*-C_5H_3N), 8.02 (t, 1H, $^3J_{H\text{-}H}$ = 6 Hz, *p*-C_5H_3N), 12.30 ppm (br, 1H, N*H*). ^{11}B{^{1}H} NMR (CD_3CN, 96 MHz, 293 K): δ -20.9 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 293 K): δ -133.9 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), -164.5 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -168.6 ppm (t, 2F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). ^{13}C{^{1}H} NMR (CD_3CN, 75 MHz, 293 K) (partial): 155.4, 149.4 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *o*-C_6F_5), 144.2, 139.2 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *m*-C_6F_5), 131.6, 129.0, 127.0, 124.3, 20.7 ppm.

Preparation of [Lut(C_4H_3S)C=C(H)B(C_6F_5)$_3$] 9

B(C_6F_5)$_3$ (0.1024 g, 0.2 mmol), Lutidine (**Lut**) (0.021 g, 0.2 mmol), 3-Ethynylthiophene (0.022 g, 0.2 mmol) were dissolved in 2 mL of toluene and allowed the orange solution to stir at 80^{o}C for 8 h. The reaction mixture was then concentrated to half of its original volume and hexane (5 mL) was added to promote precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as brown solid. Yield: 45%. Anal. Calcd for $C_{31}H_{13}BF_{15}NS$: C, 51.19; H, 1.80; N, 1.93. Found: C, 51.15; H, 1.85; N, 1.98. ^{1}H NMR (CD_3CN, 300 MHz, 293 K): δ 2.59 (s, 6H, -CH_3), 6.74 (s, 1H, =C*H*), 6.82 (m, 1H, C_4H_3S), 7.16 (d, 1H, *J* = 6 Hz, C_4H_3S), 7.19 (d, 1H, *J* = 6 Hz, C_4H_3S), 7.70 (d, 2H, $^3J_{H\text{-}H}$ = 6 Hz, *m*-C_5H_3N), 8.19 (t, 1H, $^3J_{H\text{-}H}$ = 6 Hz, *p*-C_5H_3N. ^{11}B{^{1}H} NMR (CD_3CN, 96 MHz, 293 K): δ -16.4 ppm (s). ^{19}F NMR (CD_3CN, 282 MHz, 29 3K): δ -132.8 (d, 6F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5),

-163.7 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -168.1 ppm (t, 2F, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). $^{13}C\{^1H\}$ NMR (CD_3CN, 75 MHz, 293 K) (partial): δ 157.1, 149.3 (dm, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5), 145.4, 139.4 (dm, $^1J_{C\text{-}F}$ = 243 Hz, *p*-C_6F_5), 137.4 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *m*-C_6F_5), 129.1, 128.3, 126.9, 124.3, 21.4 ppm.

Preparation of *Z*- and *E*-PhC(H)=C(C_6F_5)B(C_6F_5)$_2$ 10-*Z* and 10-*E*

$B(C_6F_5)_3$ (0.0128g, 0.025mmol) and PhC≡CH (0.0026g, 0.025mmol) were dissolved in 0.5mL of benzene-d_6 in a NMR tube, the solution turned to red. ^1H NMR (benzene-d_6, 300 MHz, 293 K): δ 7.73 (s, 1H, =C*H*, 10-*Z*), 7.59 (s, 1H, =C*H*, 10-*E*), 6.87-6.72 (m, 10H, Ph-*H*, 10-***Z*** and 10-*E*). ^{19}F NMR (benzene-d_6, 282 MHz, 293 K): δ -130.6 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5, 10-*E*-B(C_6F_5)$_2$), -131.9 (d, 4F, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5, 10-*Z*-B(C_6F_5)$_2$), -140.8 (d, 2F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5, 10-*Z*-C_6F_5), -144.4 (d, 2F, $^3J_{FF}$ = 21 Hz, *o*-C_6F_5, 10-*E*-C_6F_5), -147.4 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5, 10-*E*-B(C_6F_5)$_2$), -148.5 (t, 2F, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5, 10-*Z*-B(C_6F_5)$_2$), -156.2 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5, 10-*E*-C_6F_5), -156.6 (t, 1F, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5, 10-*Z*-C_6F_5), 162.6 (m, 4F, *m*-C_6F_5, 10-*Z* and 10-*E*-C_6F_5), 163.8 (m, 8F, *m*-C_6F_5, 10-*Z* and 10-*E*-B(C_6F_5)$_2$).

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7. Summary

Frustrated Lewis Pairs (FLPs) put forth by D. W. Stephan in 2006 demonstrated that combination of sterically encumbered Lewis acids and bases do not undergo the ubiquitous "neutralization reaction" to form classical Lewis acid-base adduct, but as encounter complexes they retain "unquenched" reactivity enabling activation of small molecules. Typical examples of FLPs are inter- or intramolecular combination of bulky phosphines or amines with strongly electrophilic $RB(C_6F_5)_2$ components. Many of FLPs are capable of activating H_2 heterolytically, and part of them could serve as metal-free catalysts to hydrogenate bulky imines, enamines or enol ethers. FLPs also react with alkenes, aldehydes and a variety of other small molecules. It is obvious that FLPs and FLP chemistry have developed from chemical curiosities into a new stretegy for the activation of a variety of small molecules. Fundamental understanding of such system will be crucial to progress in the further developments and chemical explotation of such reactions.

With the expectation that double Lewis acids (DLAs) together with bulky Lewis bases would increase the potential for H_2 activation by taking advantage of their unique bidentate geometry, we prepared the DLA, 1,8-bis(dipentafluorophenylboryl) naphthalene **1** (Chapter 2). The result showed that this compound can activate H_2 heterolytically under mild conditions in the presence of bulky Lewis bases, like 2,2,6,6-tetramethylpiperidine (**TMP**) and tri-*tert*-butylphosphine (*t*-Bu_3P). Furthermore, compund **1** proved to be a fairly good catalyst for the direct hydrogenation of sterically demanding imines. But it is not as active as $B(C_6F_5)_3$, this presumably because of its too great steric hindrance in between the two boron centers. Attempts to trace the interaction of H_2 with the double Lewis acid **1** via ^1H and ^{19}F NMR spectroscopy at temperature as low as 193 K were not successful, which might suggest that the formation a more stable and observable internal **1**-H_2 adduct has a high barrier to form, while the external **1**-H_2 adduct is relatively unstable - similar to the $B(C_6F_5)_3$ cases - and too short-lived to be identified with conventional analytical methodologies.

Besides, we also applied $RB(C_6F_5)_2$ (R = Cl, H, Cy, PhC_2H_4) as the Lewis acidic component in Frustrated Lewis pairs (FLP) chemistry (Chapter 3 and 4). With $ClB(C_6F_5)_2$ H_2 could be cleaved heterolytically in the presence of bulky Lewis bases (**TMP**, *t*Bu_3P, Mes_3P and **TTBP)** to give the $[HClB(C_6F_5)_2]^-$ anion as an intermediate, which undergoes hydride/chloride exchange with the remaining $ClB(C_6F_5)_2$ in the system to generate $[Cl_2B(C_6F_5)_2]^-$ and $[HB(C_6F_5)_2]_n$ (n = 1 or 2). The $[HB(C_6F_5)_2]_n$ molecule formed a tight Lewis adduct with **TMP**, which was unreactive toward H_2. At higher temperatures the Lewis adduct *t*Bu_3P-$BH(C_6F_5)_2$ reacted in form of its *t*$Bu_3P\cdots BH(C_6F_5)_2$ FLP with H_2 to generate the salt $[tBu_3PH][H_2B(C_6F_5)_2]$. In the presence of H_2, the FLPs $Mes_3P\cdots[HB(C_6F_5)_2]$ and **TTBP**$\cdots[HB(C_6F_5)_2]$ effected formation of the $[H_2B(C_6F_5)_2]^-$ anion as a first intermediate, which then underwent disproportionation of the substituents to form $[Mes_3PH][HB(C_6F_5)_3]$ or [**TTBP**H][$HB(C_6F_5)_3$] and the quite basic $[H_3B(C_6F_5)]^-$ anion, which was withdrawn from the disproportionation equilibrium by a reaction with the quite acidic $[Mes_3PH]^+$ and [**TTBP**H]$^+$ cations affording H_2, the Lewis base and *syn* and *anti* $[H_2B(C_6F_5)]_2$.

The Lewis acids $CyB(C_6F_5)_2$ and $PhC_2H_4B(C_6F_5)_2$, which exhibit about 15 % and about 10 % lower Lewis acidity in comparison with $B(C_6F_5)_3$, were found to uptake and release H_2 reversibly in combination with the bulky Lewis bases **TMP**, **PMP** and *t*-Bu_3P. Changes in the Lewis bases turned out to be of secondary importance for hydrogenation/dehydrogenation reversibility. The main factor for reversible activation of H_2 was found to be the diminished Lewis acidity with regard to $B(C_6F_5)_3$ accomplished by variation of one of the boron substituents.

Though an increasing number of related FLP systems were discovered after the pioneering work of Stephan et al, understanding of the mechanism of the H_2 activation by FLPs is still a great challenge. Based on the theoretical studies that the intermediate formed between H_2 and the FLP "encounter complex" can be spectroscopically detected only under the condition that a P···B distance is for instance over 4.5 Å, we explored several sterically hindered Lewis bases, mainly piperidine and pyridine derivatives, to modulate the distance between B and N in FLP complex (Chapter 5). But our studies suggested that the FLPs have the characteristic feature of structural flexibility, allowing variation of the B···N distance in a quite broad range.

Attempts to detect the LB···H_2···LA intermediate through adjustment of the distance between the donor and the acceptor remains to be a challenge. The FLP/H_2 intermediate could still not be detected.

In addition**,** We also used terminal alkynes to react with Frustrated Lewis pairs (**FLP**s). The strong Lewis acid $B(C_6F_5)_3$ and bulky Lewis bases (LB) reacted with terminal alkynes (R = H, Ar) to undergo primary heterolytic splitting of the ≡C-H bond to form $[LBH][RC{\equiv}CB(C_6F_5)_3]$ salts. For R = H the acetylide adducts can react further with additional $B(C_6F_5)_3$ and subsequent 1,2-C_6F_5 migration to yield $[LBH][B(C_6F_5)_2(C_6F_5)C{=}C(H)B(C_6F_5)_3]$. Alternatively, the FLPs undergo 1,2-addition reactions with terminal alkynes to yield donor/acceptor substituted alkenes of type $[R(LB)C{=}C(H)B(C_6F_5)_3]$.

In summary, in order to contribute to eclucidation of the mechanism of the H_2 activation by FLPs, we have employed several strong Lewis acids in FLP chemistry. All the applied Lewis acids were found to active H_2 heterolytically under mild conditions in the presence of bulky Lewis bases, but attempts to trace intermediates appearing during the activating process is still a great challenge.

8. Zusammenfassung

D. W. Stephan et al. zeigten 2006, dass Lewis Säure/Base Addukte aus sperrigen Lewis Säuren und Basen führen nicht zu Lewis Säure-Basen-Addukten. Dennoch erhalten sie einen Teil ihrer Reaktivität und können kleine Moleküle aktivieren. Die Lewis-Säure-Basen-Paare nehmen in einem Begegnungskomplex, der als „Frustrated Lewis Pair“ (FLP) bezeichnet wird, grosse Abstände ein. Die kleinen Moleküle schieben sich zur Aktivierung zwischen die Lewis-Partner. Typische Beispiele dafür sind inter- oder intramolekulare Addukte aus sterisch anspruchsvollen Phosphinen oder Aminen und $RB(C_6F_5)_2$ Gruppen. Viele FLPs sind in der Lage, H_2 heterolytisch aktivieren und einige können sogar sterisch gehinderte Imine, Enamine und Enolether katalytisch hydrieren. FLPs reagieren auch mit Alkenen, Aldehyden und einer Vielzahl anderer kleiner Moleküle. Ein fundamentales Verständnis solcher Systeme ist unabdingbar, um solche Reaktionen weiter zu entwickeln und nutzen zu können.

Mit der Erwartung, dass "doppelte Lewis Säuren" (DLAs) zusammen mit sterisch gehinderten Basen die Fähigkeit, H_2 zu aktivieren, weiter zu verbessern, synthetisierte ich die DLA 1,8-bis(dipentafluorophenylboryl)naphtalene **1** (Kapitel 2). Die Ergebnisse zeigten, dass diese Verbindung H_2 unter milden Bedingungen in der Gegenwart von Lewis Basen wie 2,2,6,6-Tetramethylpiperidin (TMP) oder tri-tert-Butylphosphin (*t*-Bu_3P) heterolytisch spaltet. Desweiteren erwies sich die Verbindung **1** als guter Katalysator für die direkte Hydrierung von sterisch gehinderten Iminen. **1** ist nicht so aktiv wie $B(C_6F_5)_3$, was vermutlich auf sterische Faktoren zurückgeführt werden kann. Versuche, die initielle Wechselwirkung zwischen H_2 und der DLA **1** mittels ^1H und ^{19}F NMR bei tiefen Temperaturen (bis –193K) nachzuweisen, waren erfolglos. Dies wies auch darauf hin, dass die Bildung eines stabileren und beobachtbaren internen H_2-Addukts mit 1 eine hohe Barriere besitzt, während das externe Addukt mit H_2 relativ instabil und zu kurzlebig ist – ähnlich wie in den Fällen mit $B(C_6F_5)_3$ als Lewis-Säure, um diese mit konventionellen analytischen Methoden identifizieren zu können.

Ausserdem verwendete ich auch $RB(C_6F_5)_2$ (R = Cl, H, Cy, PhC_2H_4) als Lewis-saure

Komponente in der FLP-Chemie (Kapitel 3 und 4). Mit $ClB(C_6F_5)_2$ konnte H_2 in der Gegenwart von sterisch gehinderten Basen (TMP, *t*-Bu_3P, Mes_3P und TTBP) heterolytisch aktiviert werden, was zur Bildung von $[HClB(C_6F_5)_2]$-Anionen führte, welche eine H/Cl-Austauschreaktion mit $ClB(C_6F_5)_2$ durchlaufen. Dies führte zur Bildung eines $[Cl_2B(C_6F_5)_2]^-$-Anions und $HB(C_6F_5)_2$. $HB(C_6F_5)_2$ bildet ein stabiles Lewis Säure/Base Addukt mit TMP, welches nicht mehr mit H_2 reagiert. Bei höheren Temperaturen reagiert das Lewis-Addukt *t*-$Bu_3P\cdots BH(C_6F_5)_2$ mit H_2 unter der Bildung eines [*t*-Bu_3PH][$H_2B(C_6F_5)_2$] Salzes. In Gegenwart von H_2 reagierten die Lewis-Addukte $Mes_3P\cdots BH(C_6F_5)_2$ und $TTBP\cdots BH(C_6F_5)_2$ zu den $[H_2B(C_6F_5)_2]^-$-Anionen, welche dann eine Substituenten-Dissproportionierung zu $[H_3B(C_6F_5)]^-$ und $[HB(C_6F_5)_3]^-$ durchlaufen. $[H_3B(C_6F_5)]^-$ ist ziemlich basisch und wird von den Kationen $[HPMes_3]^+$ und $[TTBPH]^+$ protoniert, was zur Bildung von den dinuklearen Teilchen *syn*- und *anti*-$[H_2B(C_6F_5)]_2$ und H_2 führt.

Die Lewis-Säuren $CyB(C_6F_5)_2$ und $PhC_2H_4(B(C_6F_5)$, welche eine um ca. 15%, respektive 10% niedrigere Lewis-Acidität als $B(C_6F_5)_3$ besitzen, aktivierten H_2 in der Gegenwart der sperrigen Lewis-Basen TMP, PMP und *t*-Bu_3P reversibel. Die Variation der Lewis-Basen hatte keinen grossen Einfluss auf die Reversibilität der Hydrierungsreaktion. Es zeigte sich, dass die im Vergleich zu $B(C_6F_5)_3$ kleinere Lewis-Acidität dieser Lewis-Säuren, der Hauptgrund für die Reversibilität der H_2-Aktivierung ist.

Der Pionierarbeiten von Stephan et al. haben die Entwicklung einer zunehmenden Zahl von FLP-Systemen induziert; dennoch ist der Mechanismus der H_2 Aktivierung durch FLPs experimentell bislang noch kaum erforscht. Theoretische Studien sagen einen "Begegnungskomplex" zwischen H_2 und dem FLP mit einem P···B Abstand von ca. 4.5Å voraus. Um diesen "Begegnungskomplex" spektroskopisch nachzuweisen, versuchten wir den N-B-Abstand durch Variation der Lewis-Base so zu beeinflussen, dass der "Begegnungskomplex" stabilisiert wird. Unsere Untersuchungen zeigten aber, dass die FLPs eine grosse strukturelle Flexibilität besitzen und der jeweilige N-B Abstand über einen breiten Bereich variiert werden kann. Der Versuch solche Begegnungskomplexe, der Form $LB\cdots H_2\cdots LA$, durch die Anpassung des Abstands zwischen Akzeptor (LA) und Donor (LB) so zu beeinflussen, dass sie spektroskopisch nachgewiesen werden können, bleibt somit eine

Herausforderung.

Desweiteren untersuchten wir die Aktivierung von Alkinen durch FLPs. Die starke Lewis-Säure $B(C_6F_5)_3$ und eine sperrige Lewis Base reagierten mit terminalen Alkinen unter heterolytischem C-H Bindungsbruch zu den $[(C_6F_5)_3B\text{-}C{\equiv}CR][HB]$ Salzen. Das Acetylid Addukt $[(C_6F_5)_3B\text{-}C{\equiv}CH][HLB]$ reagiert mit einem weiteren Äquivalent $B(C_6F_5)_3$ in einer 1,2-C_6F_5 Wanderung zu $[LBH][B(C_6F_5)_2(C_6F_5)C{=}CHB(C_6F_5)_3]$. Auf einem alternativen Reaktionspfad können die FLPs an die terminalen Alkine addiert werden, was zu Donor/Akzptor-substituierten Alkenen des Typs $[R(LB)C{=}C(H)(B(C_6F_5)_3]$ führt.

Mit dieser Arbeit wurde ein Beitrag dazu geleistet, den Mechanismus der H_2-Aktivierung durch FLPs zu erforschen. Es wurde eine Vielzahl Lewis-Säuren untersucht, welche alle in der Lage waren H_2 in Gegenwart einer Lewis Base unter milden Bedingungen zu aktivieren. Der Versuch Zwischenstufen dieser Reaktionen nachzuweisen, bleibt noch immer eine grosse Herausforderung.

9. Acknowledgement

It is great pleasure for me to thank those people who gave me great help during my Ph.D.

First of all, I would like to express my greatest appreciation to my supervisor Prof. Dr. Heinz Berke for giving me this opportunity to study here, for having introduced me into an interesting research field and for his excellent guidance and generous support.

I am also very grateful to the members of the group, in particular to Dr. Olivier Blacque for X-ray crystal structure analyses and DFT calculation; Dr. Thomas Fox for NMR measurements, Dr. Ferdinand Wild for MS analyses, Mr. Heinz Spring for elemental analyses, Mr. Manfredd Jöhri for his great support in hardware techniques. Also, I would like to thank Dr. Christian Frech and Dr. Koushik Venkatesan for a great deal of helpful discussion.

Furthermore, I would like to express my sincere gratitude to Ms. Beatrice Spichtig, Ms. Susanna Sprokkereef, Ms. Tanja Spörri and Nathalie Fichter for their assistance in administrative affairs and their generous help in many ways of my work and my life in Zurich.

I am grateful to all members in the group of Prof. Dr. Heinz Berke for the various help and coorperation.

Financial support from the Swiss National Science Foundation and from the funds of the University of Zurich is acknowledged.

Finally, I would like to express my appreciation to my family. Thanks my parents for their constant love and encouragement. And also thank my beloved husband, Chen Wang, for his endless love and constant encouragement all through these years. To him I dedicated this thesis.

10. Appendix

List of Abbreviations

Cy	cyclohexyl
Ph	phenyl
[]	encloses complex molecules or ions
μ	Descriptor of bridging
IR	Infrared
NMR	Nuclear Magnetic Resonance
δ	chemical shift
ν	frequency
Hz	hertz
br	broad
m	multiplet (NMR)
s	singlet (NMR)
d	doublet
t	triplet
q	quartet
T_1	spin-lattice relaxation time
TON	turn-over number
TOF	turn-over frequency
DFT	Density functional theory
ppm	part per million
h	hour(s)
min	minute(s)
s	second(s)
o-	ortho

m-	meta
p-	para
Å	angstrom unit, 10^{-10} m
Anal.Calcd.	elemental analysis calculated
TMP	2,2,6,6-tetramethylpiperidine
TTBP	2,4,6-tri-*tert*-butylpyridine
PMP	1,2,2,6,6-pentamethylpiperidine
Et-TMP	1-ethyl-2,2,6,6-tetramethylpiperidine
LUT	2,6-lutidine

11. Curriculum Vitae

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12. Publication

- **Chunfang Jiang**, Olivier Blacque, Heinz Berke, "Activation of Terminal Alkynes by Frustrated Lewis Pairs", *Organometallics*, **2010**, *29*, 1125-1133.
- **Chunfang Jiang**, Olivier Blacque, Heinz Berke, "Metal-Free Hydrogen Activation by the Frustrated Lewis Pairs of $ClB(C_6F_5)_2$ and $HB(C_6F_5)_2$ and Bulky Lewis Bases", *Organometallics*, **2009**, *28*, 5233-5239.
- **Chunfang Jiang**, Olivier Blacque, Heinz Berke, "Metal-free hydrogen activation and hydrogenation of imines by 1,8-Bis(dipentafluorophenylboryl)naphthalene", *Chem. Commun*., **2009**, 5518.
- **Chunfang Jiang**, Olivier Blacque, Thomas Fox, Heinz Berke, "Reversible, Metal-Free Hydrogen Activation by Frustrated Lewis Pairs", *Dalton Trans*, submitted.
- **Chunfang Jiang**, Olivier Blacque, Thomas Fox, Heinz Berke, "Heterolytic Cleavage of H_2 by Frustrated B/N Lewis Pairs", *Organometallics*, submitted.